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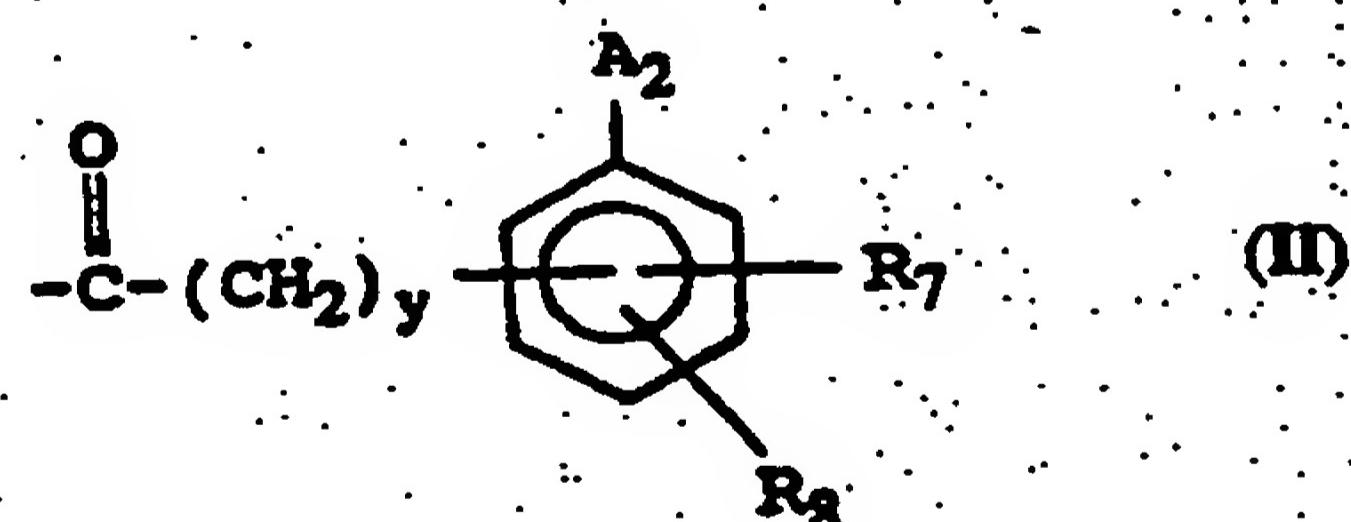
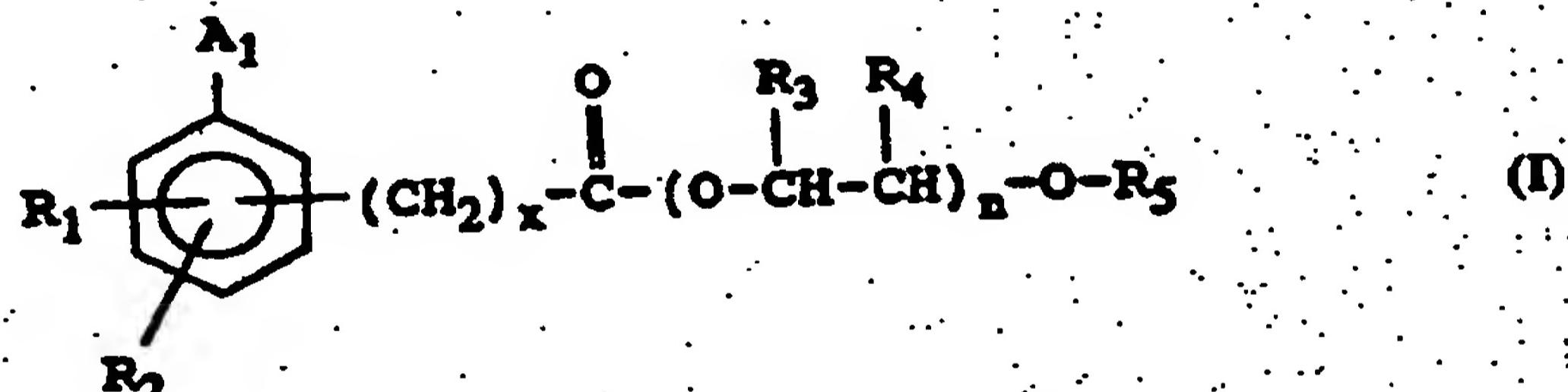
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(54) Title: FUEL COMPOSITIONS CONTAINING POLYALKYL AND POLYOXYALKYLENE AROMATIC ESTERS

(57) Abstract

A fuel additive having formula (I) wherein A_1 is a thioether, a sulfoxide, a sulfone, a sulfonic acid, a sulfonamide, a nitrile, a carboxylic acid or ester, or a carboxamide; R_1 and R_2 are independently hydrogen, hydroxy, lower alkyl or lower alkoxy; R_3 and R_4 are independently hydrogen or lower alkyl; n is an integer from 0 to 100; and when n is 0 to 10, R_5 is polyalkyl having an average molecular weight of 450 to 5,000; and when n is 5 to 100, R_5 is hydrogen, alkyl, phenyl, aralkyl, alkaryl or an acyl group having formula: (a) or (II) wherein R_6 is alkyl, phenyl, aralkyl or alkaryl; R_7 and R_8 are independently hydrogen, hydroxy, lower alkyl or lower alkoxy; A_2 is a thioether, a sulfoxide, a sulfone, a sulfonic acid, a sulfonamide, a nitrile, a carboxylic acid or ester, or a carboxamide; and x and y are independently integers from 0 to 10; with the proviso that when n and x are both 0, then A_1 may not be a carboxylic acid or ester, or a carboxamide.



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01 FUEL COMPOSITIONS CONTAINING POLYALKYL
02 AND POLY(OXYALKYLENE) AROMATIC ESTERS

03
04 BACKGROUND OF THE INVENTION

05
06 Field of the Invention

07
08 This invention relates to polyalkyl and poly(oxyalkylene)
09 aromatic esters and to fuel compositions containing
10 poly(oxyalkylene) aromatic esters. More particularly, this
11 invention relates to polyalkyl and poly(oxyalkylene)
12 aromatic esters which are substituted on the aromatic moiety
13 and to the use of such compounds in fuel compositions to
14 prevent and control engine deposits.

15
16 Description of the Related Art

17
18 It is well known that automobile engines tend to form
19 deposits on the surface of engine components, such as
20 carburetor ports, throttle bodies, fuel injectors, intake
21 ports and intake valves, due to the oxidation and
22 polymerization of hydrocarbon fuel. These deposits, even
23 when present in relatively minor amounts, often cause
24 noticeable driveability problems, such as stalling and poor
25 acceleration. Moreover, engine deposits can significantly
26 increase an automobile's fuel consumption and production of
27 exhaust pollutants. Therefore, the development of effective
28 fuel detergents or "deposit control" additives to prevent or
29 control such deposits is of considerable importance and
30 numerous such materials are known in the art.

31
32 For example, aliphatic hydrocarbon-substituted phenols are
33 known to reduce engine deposits when used in fuel
34 compositions. U.S. Patent No. 3,849,085, issued

-2-

01 November 19, 1974 to Kreuz et al., discloses a motor fuel
02 composition comprising a mixture of hydrocarbons in the
03 gasoline boiling range containing about 0.01 to 0.25 volume
04 percent of a high molecular weight aliphatic
05 hydrocarbon-substituted phenol in which the aliphatic
06 hydrocarbon radical has an average molecular weight in the
07 range of about 500 to 3,500. This patent teaches that
08 gasoline compositions containing minor amounts of an
09 aliphatic hydrocarbon-substituted phenol not only prevent or
10 inhibit the formation of intake valve and port deposits in a
11 gasoline engine, but also enhance the performance of the
12 fuel composition in engines designed to operate at higher
13 operating temperatures with a minimum of decomposition and
14 deposit formation in the manifold of the engine.
15
16 Similarly, U.S. Patent No. 4,134,846, issued January 16,
17 1979 to Machleider et al., discloses a fuel additive
18 composition comprising a mixture of (1) the reaction product
19 of an aliphatic hydrocarbon-substituted phenol,
20 epichlorohydrin and a primary or secondary mono- or
21 polyamine, and (2) a polyalkylene phenol. This patent
22 teaches that such compositions show excellent carburetor,
23 induction system and combustion chamber detergency and, in
24 addition, provide effective rust inhibition when used in
25 hydrocarbon fuels at low concentrations.
26
27 Amino phenols are also known to function as
28 detergents/dispersants, antioxidants and anti-corrosion
29 agents when used in fuel compositions. U.S. Patent
30 No. 4,320,021, issued March 16, 1982 to R. M. Lange, for
31 example, discloses amino phenols having at least one
32 substantially saturated hydrocarbon-based substituent of at
33 least 30 carbon atoms. The amino phenols of this patent are
34 taught to impart useful and desirable properties to

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01 oil-based lubricants and normally liquid fuels. Similar
02 amino phenols are disclosed in related U.S. Patent
03 No. 4,320,020, issued March 16, 1982 to R. M. Lange.
04
05 Similarly, U.S. Patent No. 3,149,933, issued September 22,
06 1964 to K. Ley et al., discloses hydrocarbon-substituted
07 amino phenols as stabilizers for liquid fuels.
08
09 U.S. Patent No. 4,386,939, issued June 7, 1983 to R. M.
10 Lange, discloses nitrogen-containing compositions prepared
11 by reacting an amino phenol with at least one 3- or
12 4-membered ring heterocyclic compound in which the hetero
13 atom is a single oxygen, sulfur or nitrogen atom, such as
14 ethylene oxide. The nitrogen-containing compositions of
15 this patent are taught to be useful as additives for
16 lubricants and fuels.
17
18 Nitro phenols have also been employed as fuel additives.
19 For example, U.S. Patent No. 4,347,148, issued August 31,
20 1982 to K. E. Davis, discloses nitro phenols containing at
21 least one aliphatic substituent having at least about
22 40 carbon atoms. The nitro phenols of this patent are
23 taught to be useful as detergents, dispersants, antioxidants
24 and demulsifiers for lubricating oil and fuel compositions.
25
26 Similarly, U.S. Patent No. 3,434,814, issued March 25, 1969
27 to M. Dubeck et al., discloses a liquid hydrocarbon fuel
28 composition containing a major quantity of a liquid
29 hydrocarbon of the gasoline boiling range and a minor amount
30 sufficient to reduce exhaust emissions and engine deposits
31 of an aromatic nitro compound having an alkyl, aryl,
32 aralkyl, alkanoyloxy, alkoxy, hydroxy or halogen
33 substituent.
34

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01 More recently, certain poly(oxyalkylene) esters have been
02 shown to reduce engine deposits when used in fuel
03 compositions. U.S. Patent No. 5,211,721, issued May 18,
04 1993 to R. L. Sung et al., for example, discloses an oil
05 soluble polyether additive comprising the reaction product
06 of a polyether polyol with an acid represented by the
07 formula RCOOH in which R is a hydrocarbyl radical having 6
08 to 27 carbon atoms. The poly(oxyalkylene) ester compounds
09 of this patent are taught to be useful for inhibiting
10 carbonaceous deposit formation, motor fuel hazing, and as
11 ORI inhibitors when employed as soluble additives in motor
12 fuel compositions.

13
14 Poly(oxyalkylene) esters of amino- and nitrobenzoic acids
15 are also known in the art. For example, U.S. Patent
16 No. 2,714,607, issued August 2, 1955 to M. Matter, discloses
17 polyethoxy esters of aminobenzoic acids, nitrobenzoic acids
18 and other isocyclic acids. These polyethoxy esters are
19 taught to have excellent pharmacological properties and to
20 be useful as anesthetics, spasmolytics, analeptics and
21 bacteriostatics. U.S. Patent Nos. 2,714,608; 2,714,609; and
22 2,714,610, all issued to M. Matter, disclose similar
23 polyethoxy esters.

24
25 Similarly, U.S. Patent No. 5,090,914, issued February 25,
26 1992 to D. T. Reardon et al., discloses poly(oxyalkylene)
27 aromatic compounds having an amino or hydrazinocarbonyl
28 substituent on the aromatic moiety and an ester, amide,
29 carbamate, urea or ether linking group between the aromatic
30 moiety and the poly(oxyalkylene) moiety. These compounds
31 are taught to be useful for modifying macromolecular species
32 such as proteins and enzymes. U.S. Patent Nos. 5,081,295;
33 5,103,039; and 5,157,099, all issued to D. T. Reardon
34

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01 et al., disclose similar poly(oxyalkylene) aromatic
02 compounds.

03
04 U.S. Patent No. 4,328,322; issued September 22, 1980 to
05 R. C. Baron, discloses amino- and nitrobenzoate esters of
06 oligomeric polyols, such as poly(ethylene) glycol. These
07 materials are used in the production of synthetic polymers
08 by reaction with a polyisocyanate. Similar materials are
09 disclosed in U.S. Patent No. 4,515,981, issued May 7, 1985
10 to K. Otani et al., and in U.S. Patent Nos. 5,039,775 and
11 5,086,153, both issued to Y. Oyaizu.

12
13 In addition, U.S. Patent No. 4,231,759, issued November 4,
14 1980 to Udelhofen et al., discloses a fuel additive
15 composition comprising the Mannich condensation product of
16 (1) a high molecular weight alkyl-substituted
17 hydroxyaromatic compound wherein the alkyl group has a
18 number average molecular weight of about 600 to about 3,000;
19 (2) an amine, and (3) an aldehyde. This patent teaches that
20 such Mannich condensation products provide carburetor
21 cleanliness when employed alone, and intake valve
22 cleanliness when employed in combination with a hydrocarbon
23 carrier fluid.

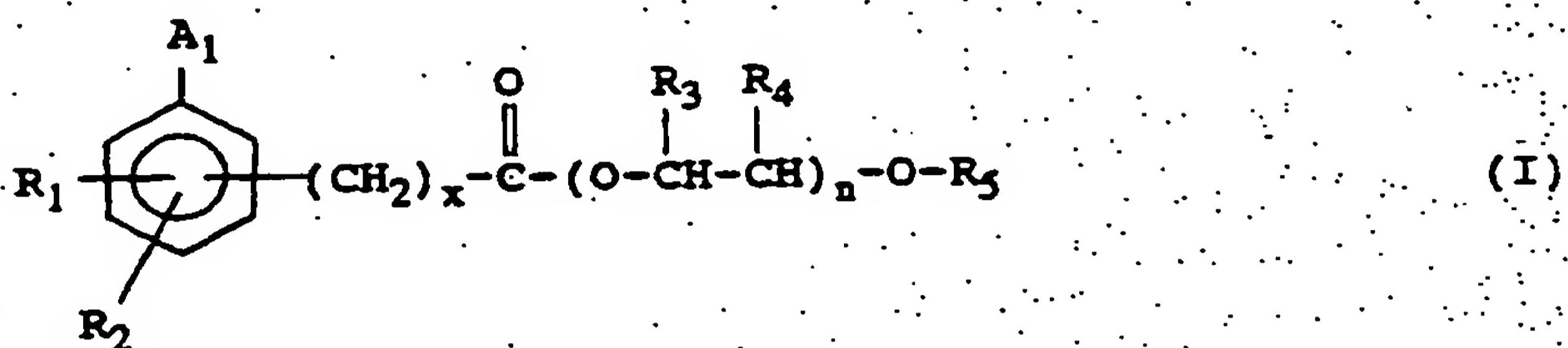
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25 U.S. Patent No. 4,859,210, issued August 22, 1989 to Franz
26 et al., discloses fuel compositions containing (1) one or
27 more polybutyl or polyisobutyl alcohols wherein the
28 polybutyl or polyisobutyl group has a number average
29 molecular weight of 324 to 3,000, or (2) a poly(alkoxylate)
30 of the polybutyl or polyisobutyl alcohol, or (3) a
31 carboxylate ester of the polybutyl or polyisobutyl alcohol.
32 This patent further teaches that when the fuel composition
33 contains an ester of a polybutyl or polyisobutyl alcohol,
34 the ester-forming acid group may be derived from saturated

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01 or unsaturated, aliphatic or aromatic, acyclic or cyclic
02 mono- or polycarboxylic acids.
03
04 U.S. Patent No. 3,285,855, issued November 15, 1966 to
05 Dexter et al., discloses alkyl esters of dialkyl
06 hydroxybenzoic and hydroxyphenylalkanoic acids wherein the
07 ester moiety contains from 6 to 30 carbon atoms. This
08 patent teaches that such esters are useful for stabilizing
09 polypropylene and other organic material normally subject to
10 oxidative deterioration. Similar alkyl esters containing
11 hindered dialkyl hydroxyphenyl groups are disclosed in U.S.
12 Patent No. 5,196,565, which issued March 23, 1993 to Ross.
13
14 U.S. Patent No. 5,196,142, issued March 23, 1993 to Mollet
15 et al., discloses alkyl esters of hydroxyphenyl carboxylic
16 acids wherein the ester moiety may contain up to 23 carbon
17 atoms. This patent teaches that such compounds are useful
18 as antioxidants for stabilizing emulsion-polymerized
19 polymers.
20
21 It has now been discovered that certain polyalkyl and
22 poly(oxyalkylene) aromatic esters which are substituted on
23 the aromatic moiety are surprisingly useful for reducing
24 engine deposits, especially intake valve deposits, when
25 employed as fuel additives in fuel compositions.
26
27 SUMMARY OF THE INVENTION
28
29 The present invention provides novel polyalkyl and
30 poly(oxyalkylene) aromatic esters which are useful as fuel
31 additives for the prevention and control of engine deposits,
32 particularly intake valve deposits.
33
34

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01 The polyalkyl and poly(oxyalkylene) aromatic esters of the
02 present invention have the formula:



wherein A₁ is selected from the group consisting of SR^I,
SOR^{II}, SO₂R^{III}, wherein R^I, R^{II} and R^{III} are independently lower
alkyl of 1 to 6 carbon atoms; SO₃H; SO₂NR^{IV}R^V, wherein R^{IV}
and R^V are independently hydrogen, lower alkyl of 1 to
6 carbon atoms or aminoalkyl of 1 to 6 carbon atoms,
provided that R^{IV} and R^V may not both be aminoalkyl; CN;
CO₂R^{VI}, wherein R^{VI} is hydrogen or lower alkyl of 1 to
6 carbon atoms; and C(O)NR^{VII}R^{VIII}, wherein R^{VII} and R^{VIII} are
independently hydrogen, lower alkyl of 1 to 6 carbon atoms
or aminoalkyl of 1 to 6 carbon atoms, provided that R^{VII} and
R^{VIII} may not both be aminoalkyl;

²³ R₁ and R₂ are independently hydrogen, hydroxy, lower alkyl
²⁴ having 1 to 6 carbon atoms, or lower alkoxy having 1 to
²⁵ 6 carbon atoms;

²⁷ R₃ and R₄ are independently hydrogen or lower alkyl having 1
²⁸ to 6 carbon atoms and each R₃ and R₄ is independently
²⁹ selected in each -O-CHR₃-CHR₄- unit;

n is an integer from 0 to 100;

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01 and when n is 0 to 10, then R₅ is a polyalkyl group having
 02 an average molecular weight in the range of about 450 to
 03 5,000;

04
 05 and when n is 5 to 100, then R₅ is hydrogen, alkyl having 1
 06 to 100 carbon atoms, phenyl, aralkyl having 7 to 100 carbon
 07 atoms, alkaryl having 7 to 100 carbon atoms, or an acyl
 08 group having the formula:

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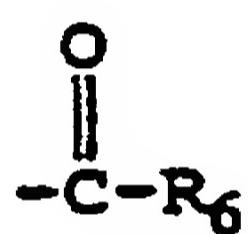
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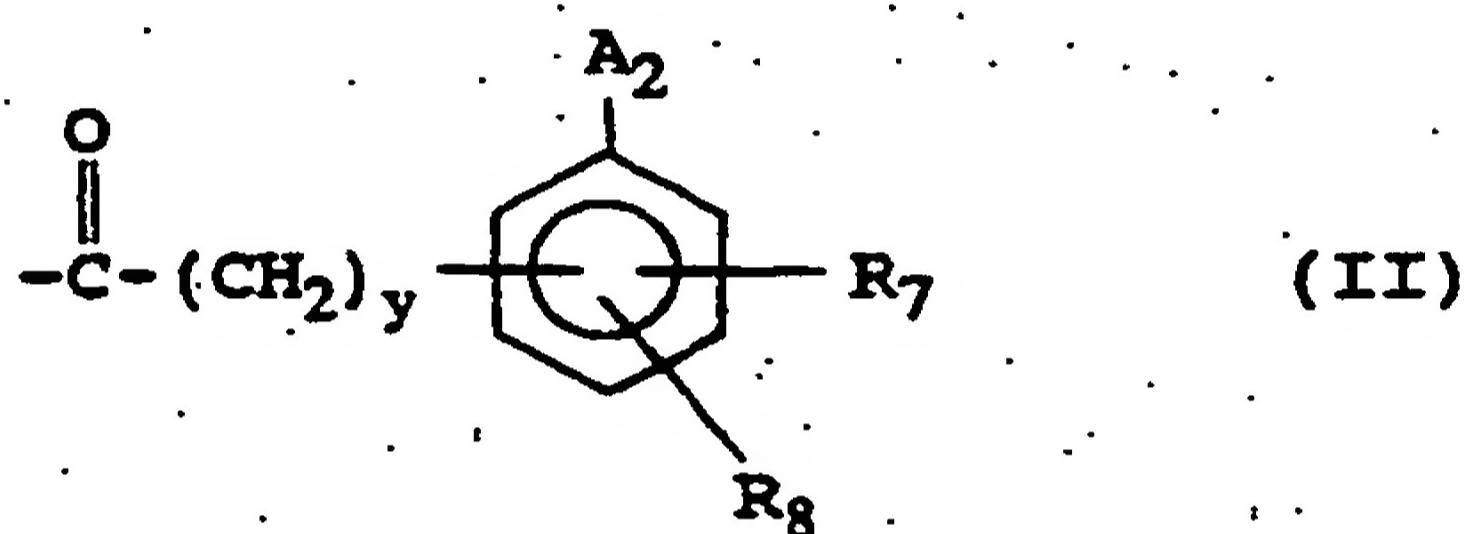
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or



wherein R₆ is alkyl having 1 to 30 carbon atoms, phenyl,
 aralkyl having 7 to 36 carbon atoms or alkaryl having 7 to
 36 carbon atoms;

R₇ and R₈ are independently hydrogen, hydroxy, lower alkyl
 having 1 to 6 carbon atoms, or lower alkoxy having 1 to
 6 carbon atoms;

A₂ is selected from the group consisting of SR^{IX}, SOR^X,
 SO₂R^{XI}, wherein R^{IX}, R^X and R^{XI} are independently lower alkyl
 of 1 to 6 carbon atoms; SO₃H; SO₂NR^{XII}R^{XIII}, wherein R^{XII} and
 R^{XIII} are independently hydrogen or lower alkyl of 1 to
 6 carbon atoms; CN; CO₂R^{XIV}, wherein R^{XIV} is hydrogen or
 lower alkyl of 1 to 6 carbon atoms; and C(O)NR^{XV}R^{XVI},
 wherein R^{XV} and R^{XVI} are independently hydrogen or lower
 alkyl of 1 to 6 carbon atoms;

-9-

01 and x and y are independently integers from 0 to 10;
02
03 with the proviso that when n and x are both 0, then A₁ may
04 not be CO₂R^{VI} or C(O)NR^{VII}R^{VIII}.

05
06 The present invention further provides a fuel composition
07 comprising a major amount of hydrocarbons boiling in the
08 gasoline or diesel range and an effective
09 deposit-controlling amount of a polyalkyl or
10 poly(oxyalkylene) aromatic ester of the present invention.

11
12 The present invention additionally provides a fuel
13 concentrate comprising an inert stable oleophilic organic
14 solvent boiling in the range of from about 150°F (65°C) to
15 400°F (205°C) and from about 10 to 70 weight percent of a
16 polyalkyl or poly(oxyalkylene) aromatic ester of the present
17 invention.

18
19 Among other factors, the present invention is based on the
20 discovery that certain polyalkyl and poly(oxyalkylene)
21 aromatic esters which are substituted on the aromatic moiety
22 are surprisingly useful for reducing engine deposits,
23 especially on intake valves, when employed as fuel additives
24 in fuel compositions.

25
26 DETAILED DESCRIPTION OF THE INVENTION

27
28 The fuel additives provided by the present invention have
29 the general formula:

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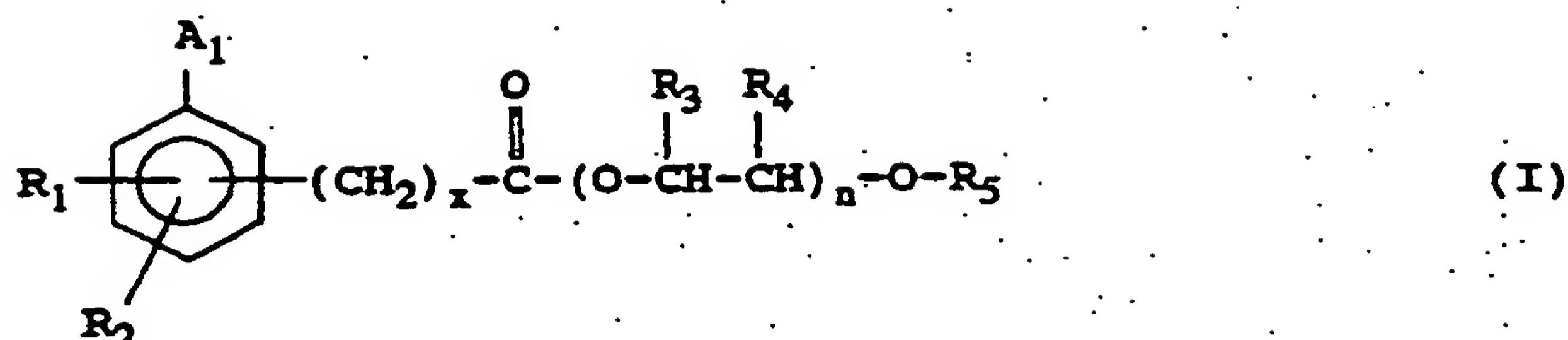
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wherein A_1 , R_1 , R_2 , R_3 , R_4 , R_5 , n and x are as defined above.

In formula I, above, A_1 may be a thioether, SR^I , a sulfoxide, SOR^{II} , a sulfone, SO_2R^{III} , a sulfonic acid, SO_3H ; a sulfonamide, $SO_2NR^{IV}R^V$, a nitrile(cyano), CN , a carboxylic acid or ester, CO_2R^{VI} , or a carboxamide, $C(O)NR^{VII}R^{VIII}$.

Preferably, A_1 is a thioether, SR^I , a sulfone, SO_2R^{III} , a nitrile, CN , a carboxylic acid or ester, CO_2R^{VI} , or a carboxamide, $C(O)NR^{VII}R^{VIII}$. More preferably, A_1 is a carboxylic acid or a carboxylic acid ester, CO_2R^{VI} , or a carboxamide, $C(O)NR^{VII}R^{VIII}$.

Preferably, R_1 is hydrogen, hydroxy, or lower alkyl having 1 to 4 carbon atoms. More preferably, R_1 is hydrogen or hydroxy. Most preferably, R_1 is hydrogen.

R_2 is preferably hydrogen.

Preferably, one of R_3 and R_4 is lower alkyl having 1 to 3 carbon atoms and the other is hydrogen. More preferably, one of R_3 and R_4 is methyl or ethyl and the other is hydrogen. Most preferably, one of R_3 and R_4 is ethyl and the other is hydrogen.

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01 The number of oxyalkylene groups, n, may range from 0 to
02 100. When n ranges from 0 to about 10 oxyalkylene groups,
03 then R₅ is a polyalkyl group having an average molecular
04 weight in the range of about 450 to 5,000, preferably in the
05 range of about 500 to 5,000, more preferably about 500 to
06 3,000, and most preferably about 600 to 2,000.

07

08 Moreover, when n ranges from about 5 to 100 oxyalkylene
09 groups, R₅ is preferably hydrogen, alkyl having 1 to
10 30 carbon atoms, or alkylphenyl having an alkyl group
11 containing 1 to 30 carbon atoms. More preferably, R₅ is
12 hydrogen, alkyl having 2 to 24 carbon atoms, or alkylphenyl
13 having an alkyl group containing 2 to 24 carbon atoms.
14 Still more preferably, R₅ is hydrogen, alkyl having 4 to
15 12 carbon atoms or alkylphenyl having an alkyl group
16 containing 4 to 12 carbon atoms. Most preferably, R₅ is
17 alkylphenyl having an alkyl group containing 4 to 12 carbon
18 atoms.
19

20

R₆ is preferably alkyl having 4 to 12 carbon atoms.

21

22 Preferably, R₇ is hydrogen, hydroxy, or lower alkyl having 1
23 to 4 carbon atoms. More preferably, R₇ is hydrogen or
24 hydroxy. Most preferably, R₇ is hydrogen.

25

R₈ is preferably hydrogen.

26

27 Preferably, A₂ is a thioether, SR^{IX}, a sulfone, SO₂R^{XI}, a
28 nitrile, CN, a carboxylic acid or ester, CO₂R^{XIV}, or a
29 carboxamide, C(O)NR^{XV}R^{XVI}. More preferably, A₂ is a
30 carboxylic acid or ester, CO₂R^{XIV}, or a carboxamide,
31 C(O)NR^{XV}R^{XVI}.

32

-12-

01 As indicated above, n is an integer from 0 to 100. In one
02 embodiment of the present invention, where R₅ is a polyalkyl
03 group having an average molecular weight of 450 to 5,000,
04 the number of oxyalkylene groups, n, will generally range
05 from 0 to about 10, preferably from 0 to about 5, and more
06 preferably, n will be 0.

07

08 In another embodiment of the present invention, where R₅ is
09 hydrogen, alkyl of 1 to 100 carbon atoms, phenyl, aralkyl of
10 7 to 100 carbon atoms, alkaryl of 7 to 100 carbon atoms or
11 an acyl group, the number of oxyalkylene groups, n, will
12 generally range from about 5 to 100, preferably from about 8
13 to 50, and more preferably, n will be an integer from about
14 10 to 30.

15

16 Preferably, x will be an integer from 0 to 2. More
17 preferably, x will be 0. Preferably, y will be an integer
18 from 0 to 2. More preferably, y will be 0.

19

20 It is especially preferred that the A₁ substituent present
21 in the aromatic moiety of the aromatic esters of this
22 invention be situated in a meta or para position relative to
23 the ester moiety. When the aromatic moiety also contains a
24 hydroxyl substituent, it is particularly preferred that this
25 hydroxyl group be in a meta or para position relative to the
26 ester moiety and in an ortho position relative to the A₁
27 substituent.

28

29 The polyalkyl and poly(oxyalkylene) aromatic esters employed
30 in the present invention will generally have a sufficient
31 molecular weight so as to be non-volatile at normal engine
32 intake valve operating temperatures (about 200-250°C).
33 Typically, the molecular weight of the polyalkyl and
34

-13-

01 poly(oxyalkylene) aromatic esters will range from about 600
02 to about 10,000, preferably from about 600 to 3,000.

03
04 Generally, the poly(oxyalkylene) aromatic esters employed in
05 this invention will contain an average of about 5 to about
06 100 oxyalkylene units; preferably, 8 to 50 oxyalkylene
07 units; more preferably, 10 to 30 oxyalkylene units.

08
09 Fuel-soluble salts of the polyalkyl and poly(oxyalkylene)
10 aromatic esters of the present invention can be readily
11 prepared for those compounds containing an amino group and
12 such salts are contemplated to be useful for preventing or
13 controlling engine deposits. Suitable salts include, for
14 example, those obtained by protonating the amino moiety with
15 a strong organic acid, such as an alkyl- or arylsulfonic
16 acid. Preferred salts are derived from toluenesulfonic acid
17 and methanesulfonic acid.

18
19 Definitions

20
21 As used herein the following terms have the following
22 meanings unless expressly stated to the contrary.

23
24 The term "alkyl" refers to both straight- and branched-chain
25 alkyl groups.

26
27 The term "lower alkyl" refers to alkyl groups having 1 to
28 about 6 carbon atoms and includes primary, secondary and
29 tertiary alkyl groups. Typical lower alkyl groups include,
30 for example, methyl, ethyl, n-propyl, isopropyl, n-butyl,
31 sec-butyl, t-butyl, n-pentyl, n-hexyl and the like.

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-14-

01 The term "lower alkoxy" refers to the group $-OR_d$ wherein R_d
02 is lower alkyl. Typical lower alkoxy groups include
03 methoxy, ethoxy, and the like.

04

05 The term "alkaryl" refers to the group:

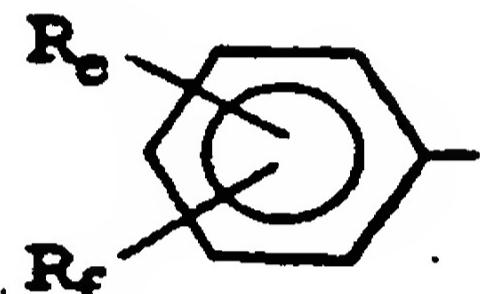
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11 wherein R_e and R_f are each independently hydrogen or an
12 alkyl group, with the proviso that both R_e and R_f are not
13 hydrogen. Typical alkaryl groups include, for example,
14 tolyl, xylyl, cumenyl, ethylphenyl, butylphenyl,
15 dibutylphenyl, hexylphenyl, octylphenyl, dioctylphenyl,
16 nonylphenyl, decylphenyl, didecylphenyl, dodecylphenyl,
17 hexadecylphenyl, octadecylphenyl, icosylphenyl,
18 tricontylphenyl and the like. The term "alkylphenyl" refers
19 to an alkaryl group of the above formula in which R_e is
20 alkyl and R_f is hydrogen.

21

22 The term "aralkyl" refers to the group:

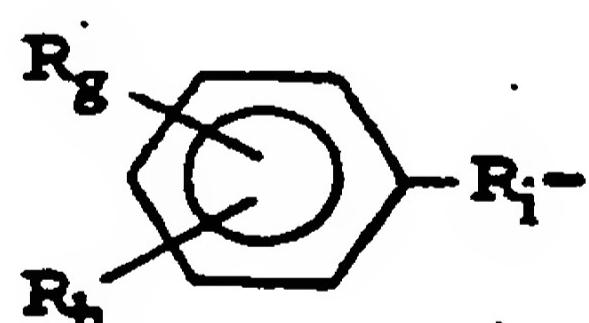
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28 wherein R_g and R_h are each independently hydrogen or an
29 alkyl group; and R_i is an alkylene group. Typical alkaryl
30 groups include, for example, benzyl, methylbenzyl,
31 dimethylbenzyl, phenethyl, and the like.

32

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-15-

01 The term "oxyalkylene unit" or "oxyalkylene group" refers to
02 an ether moiety having the general formula:

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wherein R_j and R_k are each independently hydrogen or lower alkyl groups.

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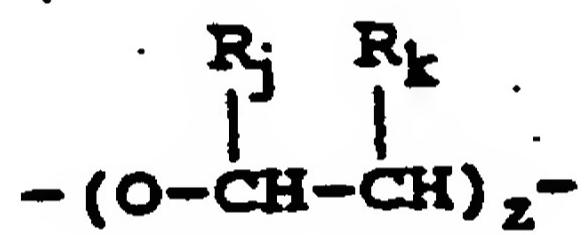
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The term "poly(oxyalkylene)" refers to a polymer or oligomer having the general formula:

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23

wherein R_j and R_k are as defined above, and z is an integer greater than 1. When referring herein to the number of poly(oxyalkylene) units in a particular poly(oxyalkylene) compound, it is to be understood that this number refers to the average number of poly(oxyalkylene) units in such compounds unless expressly stated to the contrary.

24

General Synthetic Procedures

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The polyalkyl and poly(oxyalkylene) aromatic esters employed in this invention can be prepared by the following general methods and procedures. Those skilled in the art will recognize that where typical or preferred process conditions (e.g., reaction temperatures, times, mole ratios of reactants, solvents, pressures, etc.) are given, other process conditions may also be used unless otherwise stated. Optimum reaction conditions may vary with the particular reactants or solvents used, but one skilled in the art will

-16-

01 be able to determine such conditions by routine optimization
02 procedures.

03

04 Moreover, those skilled in the art will recognize that it
05 may be necessary to block or protect certain functional
06 groups while conducting the following synthetic procedures.

07 In such cases, the protecting group will serve to protect
08 the functional group from undesired reactions or to block
09 its undesired reaction with other functional groups or with
10 the reagents used to carry out the desired chemical
11 transformations. The proper choice of a protecting group
12 for a particular functional group will be readily apparent
13 to one skilled in the art. Various protecting groups and
14 their introduction and removal are described, for example,
15 in T. W. Greene and P. G. M. Wuts, *Protective Groups in*
16 *Organic Synthesis*, Second Edition, Wiley, New York, 1991,
17 and references cited therein.

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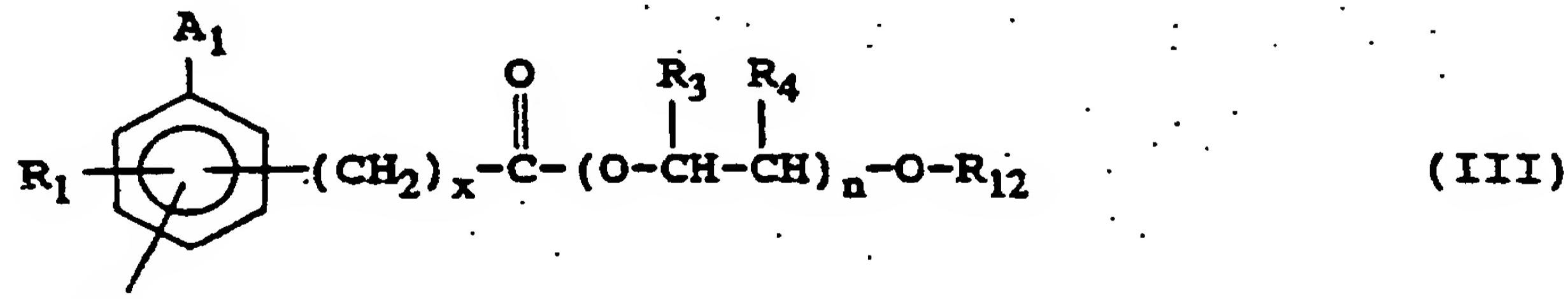
19 In the present synthetic procedures, a hydroxyl group, if
20 present, will preferably be protected, when necessary, as
21 the benzyl or tert-butyldimethylsilyl ether. Introduction
22 and removal of these protecting groups is well described in
23 the art.

24

25 The polyalkyl and poly(oxyalkylene) aromatic esters of the
26 present invention having the formula:

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-17-

01 wherein A₁, R₁-R₄, n and x are as defined above and R₁₂ is an
02 alkyl, phenyl, aralkyl, alkaryl or polyalkyl group, may be
03 prepared by esterifying an aromatic carboxylic acid having
04 the formula:

05

06

07

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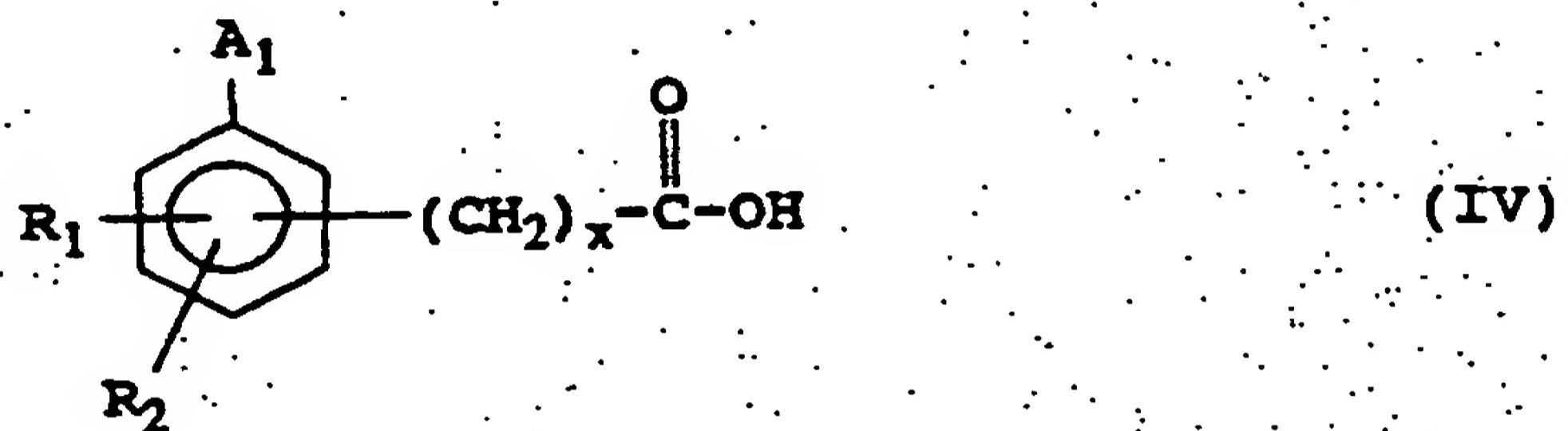
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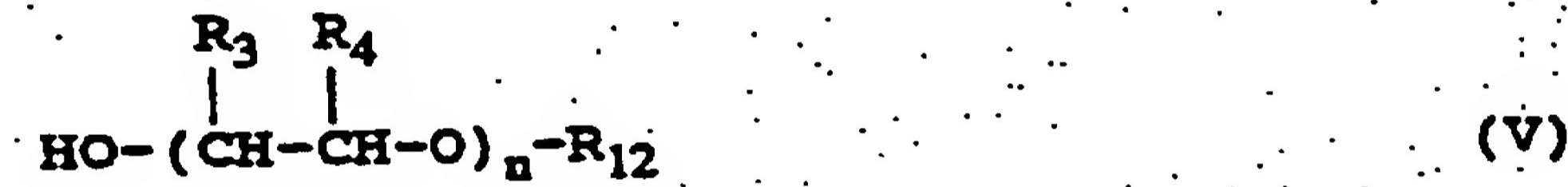
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wherein n is 0 to 100 and R₃, R₄ and R₁₂ are as defined above, using conventional esterification reaction conditions.

This reaction is typically conducted by contacting the alcohol V with about 0.25 to about 1.5 molar equivalents of aromatic carboxylic acid IV in the presence of an acidic catalyst at a temperature in the range of 70°C to about 160°C for about 0.5 to about 48 hours. Suitable acid catalysts for this reaction include, for example, p-toluenesulfonic acid, methanesulfonic acid, sulfuric acid and the like. The reaction may be conducted in the presence or absence of an inert solvent, such as toluene, xylene and the like. The water generated during this reaction may be continuously removed by conventional procedures, such as

-18-

- 01 azeotropic distillation with an inert solvent, such as
02 xylene.
03
04 Alternatively, the polyalkyl and poly(oxyalkylene) aromatic
05 esters of formula III may be prepared by reacting the
06 alcohol V with an acid halide derived from aromatic
07 carboxylic acid IV, such as an acid chloride or acid
08 bromide.
09
10 Generally, the carboxylic acid moiety of IV may be converted
11 into an acyl halide moiety by contacting IV with an
12 inorganic acid halide, such as thionyl chloride, phosphorous
13 trichloride, phosphorous tribromide, or phosphorous
14 pentachloride; or with oxalyl chloride. Typically, this
15 reaction will be conducted using about 1 to 5 molar
16 equivalents of the inorganic acid halide or oxalyl chloride,
17 either neat or in an inert solvent, such as diethyl ether,
18 at a temperature in the range of about 20°C to about 80°C
19 for about 1 to about 48 hours. A catalyst, such as
20 N,N-dimethylformamide, may also be used in this reaction.
21
22 Reaction of the acid halide derived from IV with the alcohol
23 V provides a polyalkyl or poly(oxyalkylene) aromatic ester
24 of formula III. Typically, this reaction is conducted by
25 contacting alcohol V with about 0.25 to about 1.5 molar
26 equivalents of the acid halide in an inert solvent, such as
27 toluene, dichloromethane, diethyl ether, and the like, at a
28 temperature in the range of about 25°C to about 150°C. The
29 reaction is generally complete in about 0.5 to about
30 48 hours. Preferably, the reaction is conducted in the
31 presence of a sufficient amount of an amine capable of
32 neutralizing the acid generated during the reaction, such as
33 triethylamine, di(isopropyl)ethylamine, pyridine or
34 4-dimethylaminopyridine.

01 The aromatic carboxylic acids of formula IV employed in the
02 above-described procedures are either known compounds or can
03 be prepared from known compounds by conventional procedures.
04 Representative aromatic carboxylic acids suitable for use in
05 these reactions include, for example, 4-methylthiobenzoic
06 acid, 4-methylsulfoxybenzoic acid, 4-methylsulfonylbenzoic
07 acid, 4-cyanobenzoic acid, mono-methyl terephthalic acid,
08 4-carboxybenzenesulfonamide, 4-carboxybenzenesulfonic acid,
09 and the like.

10

11 Preferred aromatic carboxylic acids include
12 4-methylthiobenzoic acid, 4-methylsulfonylbenzoic acid,
13 4-cyanobenzoic acid, and mono-methyl terephthalic acid.

14

15 Alternatively, substituent A₁ can be further modified by
16 conventional procedures well known to those skilled in the
17 art to provide additional aromatic compounds encompassed by
18 formula III, above.

19

20 The alcohols of formula V, above, will include polyalkyl
21 alcohols, R₁₂OH, where the number of oxyalkylene groups, n,
22 is 0 and R₁₂ is polyalkyl.

23

24 The polyalkyl alcohols for formula V having no oxyalkylene
25 groups may be prepared by conventional procedures known in
26 the art. Such procedures are taught, for example, in U.S.
27 Patent Nos. 5,055,607 to Buckley and 4,859,210 to Franz
28 et al., the disclosures of which are incorporated herein by
29 reference.

30

31 In general, the polyalkyl substituent on the polyalkyl
32 alcohols of formula V and the resulting polyalkyl aromatic
33 esters of the present invention will have an average
34

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01 molecular weight in the range of about 450 to 5,000,
02 preferably about 500 to 5,000, more preferably about 500 to
03 3,000, and most preferably about 600 to 2,000.

04

05 The polyalkyl substituent on the polyalkyl alcohols employed
06 in the invention may be generally derived from polyolefins
07 which are polymers or copolymers of mono-olefins,
08 particularly 1-mono-olefins, such as ethylene, propylene,
09 butylene, and the like. Preferably, the mono-olefin
10 employed will have 2 to about 24 carbon atoms, and more
11 preferably, about 3 to 12 carbon atoms. More preferred
12 mono-olefins include propylene, butylene, particularly
13 isobutylene, 1-octene and 1-decene. Polyolefins prepared
14 from such mono-olefins include polypropylene, polybutene,
15 especially polyisobutene, and the polyalphaolefins produced
16 from 1-octene and 1-decene.

17

18 The preferred polyisobutenes used to prepare the presently
19 employed polyalkyl alcohols are polyisobutenes which
20 comprise at least about 20% of the more reactive
21 methylvinylidene isomer, preferably at least 50%, and more
22 preferably at least 70%. Suitable polyisobutenes include
23 those prepared using BF_3 catalysts. The preparation of such
24 polyisobutenes in which the methylvinylidene isomer
25 comprises a high percentage of the total composition is
26 described in U.S. Patent Nos. 4,152,499 and 4,605,808. Such
27 polyisobutenes, known as "reactive" polyisobutenes, yield
28 high molecular weight alcohols in which the hydroxyl group
29 is at or near the end of the hydrocarbon chain.

30

31 Examples of suitable polyisobutenes having a high
32 alkylvinylidene content include Ultravis 30, a polyisobutene
33 having a molecular weight of about 1300 and a
34

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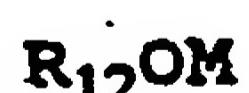
01 methylvinylidene content of about 74%; and Ultravis 10, a
02 polyisobutene having a molecular weight of about 950 and a
03 methylvinylidene content of about 76%, both available from
04 British Petroleum.

05
06 The polyalkyl alcohols may be prepared from the
07 corresponding olefins by conventional procedures. Such
08 procedures include hydration of the double bond to give an
09 alcohol. Suitable procedures for preparing such long-chain
10 alcohols are described in I. T. Harrison and S. Harrison,
11 *Compendium of Organic Synthetic Methods*, Wiley-Interscience,
12 New York (1971), pp. 119-122, as well as in U.S. Patent
13 Nos. 5,055,607 and 4,859,210.

14
15 The alcohols of formula V, above, will also include
16 poly(oxyalkylene) alcohols, where the number of oxyalkylene
17 units, n, is greater than 0, that is, from 1 to about 100.

18
19 The poly(oxyalkylene) alcohols of formula V are also known
20 compounds that can be prepared using conventional
21 procedures. For example, suitable procedures for preparing
22 such compounds are taught in U.S. Patent Nos. 2,782,240 and
23 2,841,479, the disclosures of which are incorporated herein
24 by reference.

25
26 Preferably, the poly(oxyalkylene) alcohols of formula V are
27 prepared by contacting an alkoxide or phenoxide metal salt
28 having the formula:



(VI)

29
30
31
32 wherein R_{12} is as defined above and M is a metal cation,
33 such as lithium, sodium, potassium and the like, with about
34

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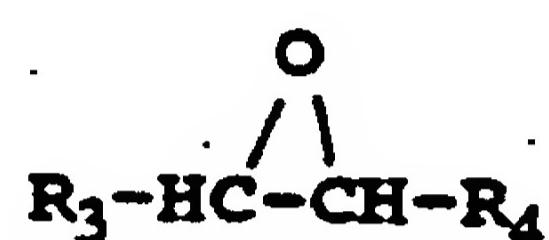
01 1 to about 100 molar equivalents of an alkylene oxide (an
02 epoxide) having the formula:

03

04

05

06



(VII)

07 wherein R₃ and R₄ are as defined above.
08

09

10 Typically, metal salt VI is prepared by contacting the
11 corresponding hydroxy compound R₁₂OH with a strong base,
12 such as sodium hydride, potassium hydride, sodium amide and
13 the like, in an inert solvent, such as toluene, xylene and
14 the like, under substantially anhydrous conditions at a
15 temperature in the range from about -10°C to about 120°C for
16 about 0.25 to about 3 hours.

17

18 Metal salt VI is generally not isolated, but is reacted in
19 situ with alkylene oxide VII to provide, after
20 neutralization, the poly(oxyalkylene) alcohol V. This
21 polymerization reaction is typically conducted in a
22 substantially anhydrous inert solvent at a temperature of
23 about 30°C to about 150°C for about 2 to about 120 hours.
24 Suitable solvents for this reaction, include toluene, xylene
25 and the like. Typically, the reaction is conducted at a
26 pressure sufficient to contain the reactants and the
27 solvent, preferably at atmospheric or ambient pressure.

28

29 The amount of alkylene oxide employed in this reaction will
30 generally depend on the number of oxyalkylene units desired
31 in the product. Typically, the molar ratio of alkylene
32 oxide VII to metal salt VI will range from about 1:1 to
33 100:1, preferably from 5:1 to about 100:1, more preferably
34 from 8:1 to 50:1, and most preferably from 10:1 to 30:1.

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01 Alkylene oxides suitable for use in this polymerization
02 reaction include, for example, ethylene oxide; propylene
03 oxide; butylene oxides, such as 1,2-butylene oxide
04 (1,2-epoxybutane) and 2,3-butylene oxide (2,3-epoxybutane);
05 pentylene oxides; hexylene oxides; octylene oxides and the
06 like. Preferred alkylene oxides are propylene oxide and
07 1,2-butylene oxide.

08
09 In the polymerization reaction, a single type of alkylene
10 oxide may be employed, e.g., propylene oxide, in which case
11 the product is a homopolymer, e.g., a poly(oxypropylene)
12 polymer. Copolymers are equally satisfactory and random
13 copolymers can be prepared by contacting metal salt VI with
14 a mixture of alkylene oxides, such as a mixture of propylene
15 oxide and 1,2-butylene oxide, under polymerization
16 conditions. Copolymers containing blocks of oxyalkylene
17 units are also suitable for use in this invention. Block
18 copolymers can be prepared by contacting metal salt VI with
19 first one alkylene oxide, then others in any order, or
20 repetitively, under polymerization conditions.

21
22 Poly(oxyalkylene) copolymers prepared by terminating or
23 capping the poly(oxyalkylene) moiety with 1 to
24 10 oxyethylene units, preferably 2 to 5 oxyethylene units,
25 are particularly useful in the present invention, since
26 these copolymers have been found to be more readily
27 esterified than those having an alkyl branch in the terminal
28 oxyalkylene unit. These copolymers may be prepared by
29 contacting metal salt IV with an alkylene oxide of formula
30 VII, such as 1,2-butylene oxide or propylene oxide, under
31 polymerization conditions and then capping or terminating
32 the resulting block of oxyalkylene units with oxyethylene
33 units by adding ethylene oxide.

34

-24-

01 The poly(oxyalkylene) alcohol V may also be prepared by
 02 living or immortal polymerization as described by S. Inoue
 03 and T. Aida in *Encyclopedia of Polymer Science and*
04 Engineering, Second Edition, Supplemental Volume, J. Wiley
 05 and Sons, New York, pages 412-420 (1989). These procedures
 06 are especially useful for preparing poly(oxyalkylene)
 07 alcohols of formula V in which R₃ and R₄ are both alkyl
 08 groups.

09

10 As noted above, the alkoxide or phenoxide metal salt VI used
 11 in the above procedures is generally derived from the
 12 corresponding hydroxy compound, R₁₂OH. Suitable hydroxy
 13 compounds include straight- or branched-chain aliphatic
 14 alcohols having 1 to about 100 carbon atoms and phenols
 15 having the formula:

16

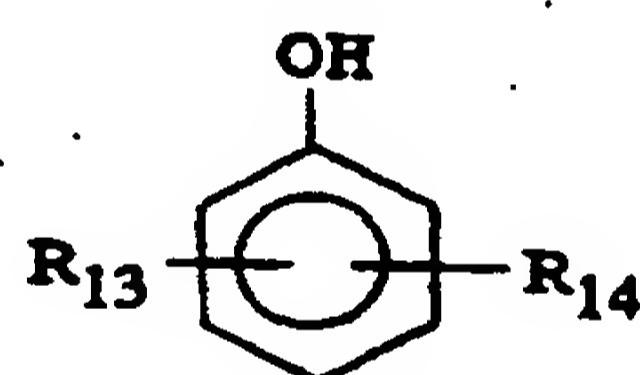
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(VIII)

22

23 wherein R₁₃ is an alkyl group having 1 to about 100 carbon
 24 atoms and R₁₄ is hydrogen; or R₁₃ and R₁₄ are both alkyl
 25 groups, each independently containing 1 to about 50 carbon
 atoms.

26

27

28 Representative examples of straight- or branched-chain
 29 aliphatic alcohols suitable for use in this invention
 30 include, but are not limited to, n-butanol; isobutanol;
 31 sec-butanol; t-butanol; n-pentanol; n-hexanol; n-heptanol;
 32 n-octanol; iso-octanol; n-nonanol; n-decanol; n-dodecanol;
 33 n-hexadecanol (cetyl alcohol); n-octadecanol (stearyl
 34 alcohol); alcohols derived from linear C₁₀ to C₃₀ alpha

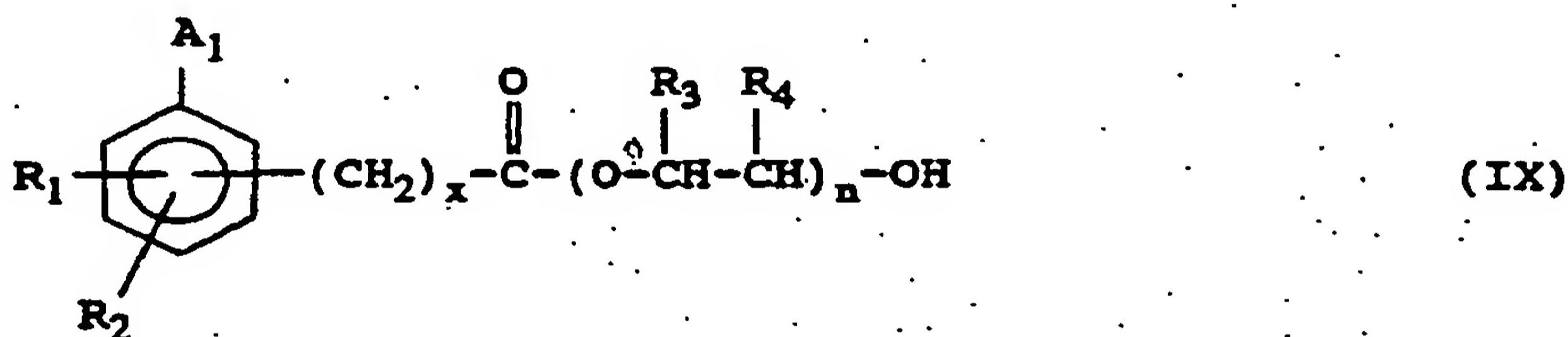
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01 olefins and mixtures thereof; and alcohols derived from
02 polymers of C₂ to C₆ olefins, such as alcohols derived from
03 polypropylene and polybutene, including polypropylene
04 alcohols having 9 to about 100 carbon atoms and polybutylene
05 alcohols having 12 to about 100 carbon atoms. Preferred
06 straight- or branched-chain aliphatic alcohols will contain
07 1 to about 30 carbon atoms, more preferably 2 to about
08 24 carbon atoms, and most preferably 4 to 12 carbon atoms.
09 Particularly preferred aliphatic alcohols are butanols.
10
11 The phenols of formula VIII may be monoalkyl-substituted
12 phenols or dialkyl-substituted phenols. Monoalkyl-
13 substituted phenols are preferred, especially
14 monoalkylphenols having an alkyl substituent in the para
15 position.
16
17 Preferably, the alkyl group of the alkylphenol will contain
18 1 to about 30 carbon atoms, more preferably 2 to 24 carbon
19 atoms, and most preferably 4 to 12 carbon atoms.
20 Representative examples of phenols suitable for use in this
21 invention include, but are not limited to, phenol,
22 methylphenol, dimethylphenol, ethylphenol, butylphenol,
23 octylphenol, decylphenol, dodecylphenol, tetradecylphenol,
24 hexadecylphenol, octadecylphenol, eicosylphenol,
25 tetracosylphenol, hexacosylphenol, triacontylphenol and the
26 like. Also, mixtures of alkylphenols may be employed, such
27 as a mixture of C₁₄-C₁₈ alkylphenols, a mixture of C₁₈-C₂₄
28 alkylphenols, a mixture of C₂₀-C₂₄ alkylphenols, or a mixture
29 of C₁₆-C₂₆ alkylphenols.
30
31 Particularly preferred alkylphenols are prepared by
32 alkylating phenol with polymers or oligomers of C₃ to C₆
33 olefins, such as polypropylene or polybutene. These
34

-26-

01 polymers typically contain 8 to about 100 carbon atoms,
02 preferably 10 to 30 carbon atoms. An especially preferred
03 alkylphenol is prepared by alkylating phenol with a
04 propylene polymer having an average of four units. This
05 polymer has the common name of propylene tetramer and is
06 commercially available.

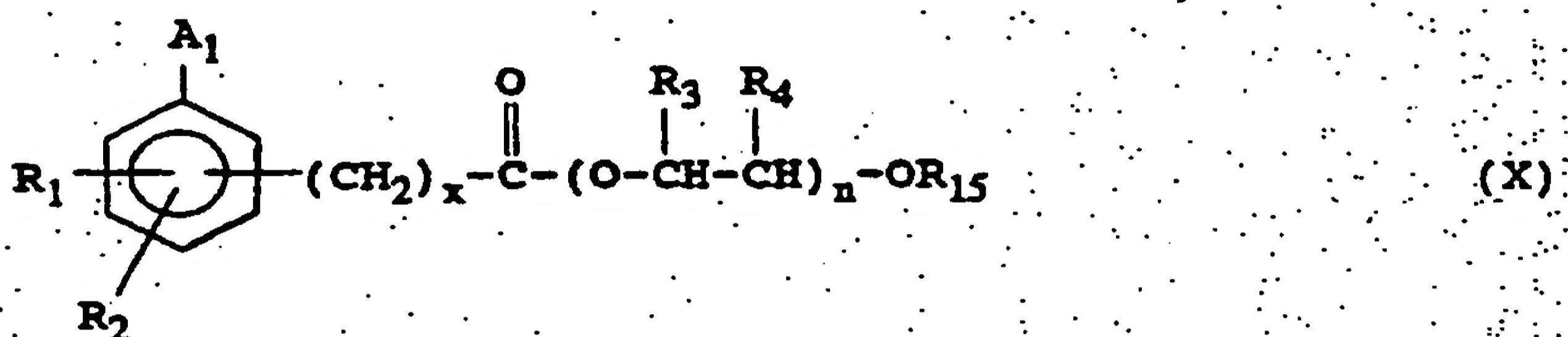
08 The poly(oxyalkylene) aromatic esters of formula I wherein
09 R₁ is hydrogen, i.e., compounds having the formula:



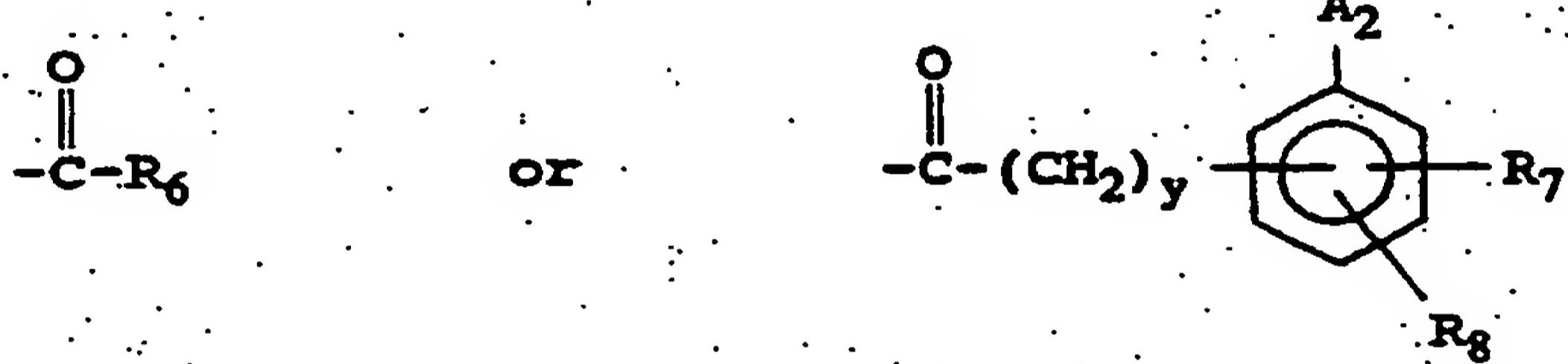
wherein A₁, R₁-R₄, n and x are as defined above, may be prepared from compounds of formula III wherein R₁₂ is a labile hydrocarbyl group, such as a benzyl or t-butyl group, by removing the hydrocarbyl group under appropriate conditions to provide a hydroxyl group. For example, compounds of formula III where R₁₂ represents a benzyl group may be prepared by employing a metal salt VI derived from benzyl alcohol in the above-described synthetic procedures. Cleavage of the benzyl ether using conventional hydrogenolysis procedures then provides a compound of formula IX. Other labile hydrocarbyl groups, such as a t-butyl group, may be similarly employed for those compounds having functional groups that are not compatible with hydrogenolysis conditions, such as nitro groups. t-Butyl ethers may be cleaved under acidic conditions using, for example, trifluoroacetic acid.

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01 The poly(oxyalkylene) aromatic esters of formula I wherein
 02 R₅ is an acyl group, i.e., compounds having the formula:



wherein A₁, R₁-R₄, n and x are as defined above and R₁₅ is an acyl group having the formula:



wherein A₂, R₆-R₈ and y are as defined above, may be synthesized from a compound of formula IX by acylating the terminal hydroxyl group of the poly(oxyalkylene) moiety with a suitable acylating agent.

Acylation agents suitable for use in this reaction include acid halides, such as acid chlorides and bromides; and carboxylic acid anhydrides. Preferred acylating agents include those having the formula: R₆C(O)-X, wherein R₆ is alkyl having 1 to 30, preferably 4 to 12 carbon atoms, phenyl, aralkyl having 7 to 36 carbon atoms or alkaryl having 7 to 36 carbon atoms, and X is chloro or bromo; and the acid halide derivatives of aromatic carboxylic acid IV described hereinabove.

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01 Representative examples of preferred acylating agents having
 02 the formula $R_6C(O)-X$ include acetyl chloride, propionyl
 03 chloride, butanoyl chloride, pivaloyl chloride, octanoyl
 04 chloride, decanoyl chloride and the like.

05

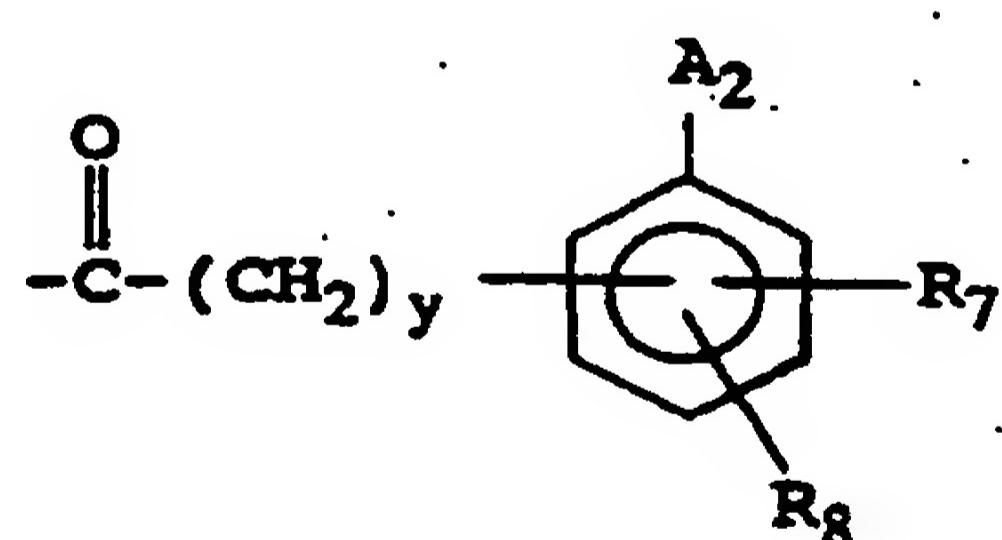
06 Typically, acylation of IX is conducted by contacting IX
 07 with about 0.95 to about 1.2 molar equivalents of the
 08 acylating agent in an inert solvent, such as toluene,
 09 dichloromethane, diethyl ether and the like, at a
 10 temperature in the range of about 25°C to about 150°C for
 11 about 0.5 to about 48 hours. When an acid halide is
 12 employed as the acylating agent, the reaction is preferably
 13 conducted in the presence of a sufficient amount of an amine
 14 capable of neutralizing the acid generated during the
 15 reaction, such as triethylamine, di(isopropyl)ethylamine,
 16 pyridine or 4-dimethylamino pyridine.

17

18 A preferred group of poly(oxyalkylene) aromatic esters of
 19 formula X are those having the same aromatic ester group at
 20 each end of the poly(oxyalkylene) moiety, i.e., compounds of
 21 formula X wherein R_{15} is an acyl group having the formula:

22

23



24

25

26

27

28

29

30 wherein $A_2 = A_1$; $R_7 = R_1$; $R_8 = R_2$; and x and y are the same
 31 integer.

32

33 These compounds may be prepared from a poly(oxyalkylene)
 34 diol having the formula:

-29-



wherein R₃, R₄, and n are as defined above, by esterifying each of the hydroxyl groups present in XI with a aromatic carboxylic acid of formula IV or an acyl halide derivative thereof using the above-described synthetic procedures. The poly(oxyalkylene) diols of formula XI are commercially available or may be prepared by conventional procedures, for example, by using sodium or potassium hydroxide in place of the alkoxide or phenoxide metal salt VI in the above-described alkylene oxide polymerization reaction.

Fuel Compositions

The polyalkyl and poly(oxyalkylene) aromatic esters of the present invention are useful as additives in hydrocarbon fuels to prevent and control engine deposits, particularly intake valve deposits. Typically, the desired deposit control is achieved by operating an internal combustion engine with a fuel composition containing a polyalkyl or poly(oxyalkylene) aromatic ester of the present invention. The proper concentration of additive necessary to achieve the desired level of deposit control varies depending upon the type of fuel employed, the type of engine, and the presence of other fuel additives.

In general, the concentration of the polyalkyl and poly(oxyalkylene) aromatic esters of this invention in hydrocarbon fuel will range from about 50 to about 2500 parts per million (ppm) by weight, preferably from 75 to 1,000 ppm. When other deposit control additives are

-30-

- 01 present, a lesser amount of the present additive may be
02 used.
- 03
- 04 The polyalkyl and poly(oxyalkylene) aromatic esters of the
05 present invention may also be formulated as a concentrate
06 using an inert stable oleophilic (i.e., dissolves in
07 gasoline) organic solvent boiling in the range of about
08 150°F to 400°F (about 65°C to 205°C). Preferably, an
09 aliphatic or an aromatic hydrocarbon solvent is used, such
10 as benzene, toluene, xylene or higher-boiling aromatics or
11 aromatic thinners. Aliphatic alcohols containing about 3 to
12 8 carbon atoms, such as isopropanol, isobutylcarbinol,
13 n-butanol and the like, in combination with hydrocarbon
14 solvents are also suitable for use with the present
15 additives. In the concentrate, the amount of the additive
16 will generally range from about 10 to about 70 weight
17 percent, preferably 10 to 50 weight percent, more preferably
18 from 20 to 40 weight percent.
- 19
- 20 In gasoline fuels, other fuel additives may be employed with
21 the additives of the present invention, including, for
22 example, oxygenates, such as t-butyl methyl ether, antiknock
23 agents, such as methylcyclopentadienyl manganese
24 tricarbonyl, and other dispersants/detergents, such as
25 hydrocarbyl amines, hydrocarbyl poly(oxyalkylene) amines, or
26 succinimides. Additionally, antioxidants, metal
27 deactivators and demulsifiers may be present.
- 28
- 29 In diesel fuels, other well-known additives can be employed,
30 such as pour point depressants, flow improvers, cetane
31 improvers, and the like.
- 32
- 33 A fuel-soluble, nonvolatile carrier fluid or oil may also be
34 used with the polyalkyl and poly(oxyalkylene) aromatic

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01 esters of this invention. The carrier fluid is a chemically
02 inert hydrocarbon-soluble liquid vehicle which substantially
03 increases the nonvolatile residue (NVR), or solvent-free
04 liquid fraction of the fuel additive composition while not
05 overwhelmingly contributing to octane requirement increase.
06 The carrier fluid may be a natural or synthetic oil, such as
07 mineral oil, refined petroleum oils, synthetic polyalkanes
08 and alkenes, including hydrogenated and unhydrogenated
09 polyalphaolefins, synthetic polyoxyalkylene-derived oils,
10 such as those described, for example, in U.S. Patent
11 No. 4,191,537 to Lewis, and polyesters, such as those
12 described, for example, in U.S. Patent Nos. 3,756,793 and
13 5,004,478 to Robinson and Vogel et al., respectively, and in
14 European Patent Application Nos. 356,726 and 382,159,
15 published March 7, 1990 and August 16, 1990, respectively.

16
17 These carrier fluids are believed to act as a carrier for
18 the fuel additives of the present invention and to assist in
19 removing and retarding deposits. The carrier fluid may also
20 exhibit synergistic deposit control properties when used in
21 combination with a polyalkyl or poly(oxyalkylene) aromatic
22 ester of this invention.

23
24 The carrier fluids are typically employed in amounts ranging
25 from about 100 to about 5000 ppm by weight of the
26 hydrocarbon fuel, preferably from 400 to 3000 ppm of the
27 fuel. Preferably, the ratio of carrier fluid to deposit
28 control additive will range from about 0.5:1 to about 10:1,
29 more preferably from 1:1 to 4:1, most preferably about 2:1.

30
31 When employed in a fuel concentrate, carrier fluids will
32 generally be present in amounts ranging from about 20 to
33 about 60 weight percent, preferably from 30 to 50 weight
34 percent.

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01

EXAMPLES

02

03 The following examples are presented to illustrate specific
04 embodiments of the present invention and synthetic
05 preparations thereof; and therefore these examples should
06 not be interpreted as limitations upon the scope of this
07 invention.

08

09

Example 1

10

11

Preparation of 4-Methylthiobenzoyl Chloride

12

13 To a flask equipped with a magnetic stirrer and a drying
14 tube was added 10.0 grams of 4-methylthiobenzoic acid,
15 150 mL of anhydrous dichloromethane, and then 13 mL of
16 oxalyl chloride. The resulting mixture was stirred at room
17 temperature for 16 hours and then the solvents removed
18 in vacuo to yield 13.1 grams of the desired acid chloride as
19 an orange yellow solid.

20

21

Example 2

22

23

Preparation of 4-Methylsulfonylbenzoyl Chloride

24

25

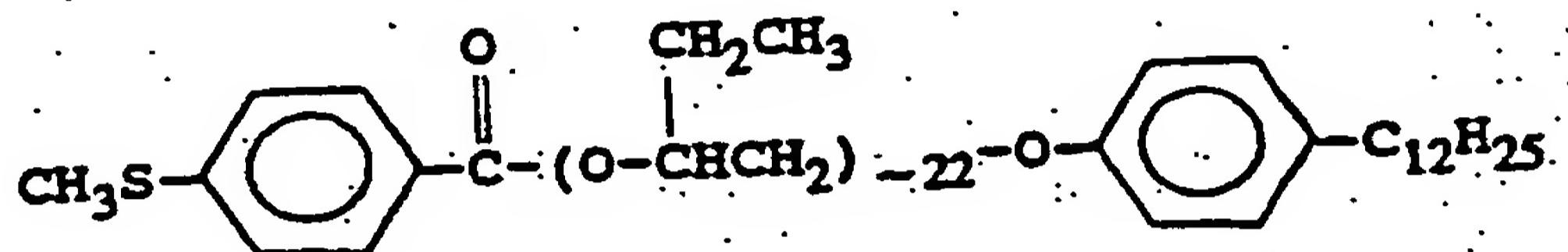
26 To a flask equipped with a magnetic stirrer and a drying
27 tube was added 10.0 grams of 4-methylsulfonylbenzoic acid,
28 150 mL of anhydrous dichloromethane, and then 10.9 mL of
29 oxalyl chloride. 1 mL of anhydrous N,N-dimethylformamide
30 was then added. The resulting mixture was stirred at room
31 temperature for 16 hours and then the solvents removed
32 in vacuo to yield 12.8 grams of the desired acid chloride as
33 a light yellow solid.

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-33-

Example 3

Preparation of α -(4-Methylthiobenzoyl)- ω - 4-dodecylphenoxy poly(oxybutylene)

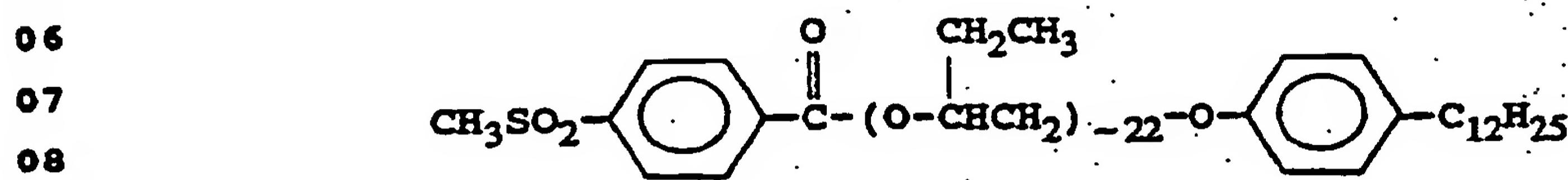


10 4-Methylthiobenzoyl chloride (13.1 grams, from Example 1)
11 was combined with 123.3 grams of α -hydroxy- ω -4-
12 dodecylphenoxy poly(oxybutylene) having an average of
13 22 oxybutylene units (prepared essentially as described in
14 Example 6 of U.S. Patent No. 4,160,648) and 500 mL of
15 anhydrous toluene. Triethylamine (9.8 mL) and
16 4-dimethylamino pyridine (4.08 grams) were then added and
17 the resulting mixture was heated to reflux under nitrogen
18 for 16 hours. The reaction was cooled to room temperature
19 and diluted with 1 liter of diethyl ether. The organic
20 layer was then washed with 1% aqueous hydrochloric acid,
21 twice with saturated aqueous sodium bicarbonate solution,
22 and once with saturated aqueous sodium chloride. The
23 organic layer was then dried over anhydrous magnesium
24 sulfate, filtered and the solvents removed in vacuo to yield
25 122.1 grams of the desired product as a brown oil. The oil
26 was chromatographed on silica gel, eluting with hexane/ethyl
27 acetate/ethanol (90:8:2) to afford 60.0 grams of the desired
28 product as a yellow oil. The product had an average of
29 22 oxybutylene units. ^1H NMR (CDCl_3) δ 7.95, 7.3 (AB
30 quartet, 4H), 7.1-7.3 (m, 2H), 6.75-6.95 (m, 2H), 5.05-5.2
31 (m, 1H), 3.85-4.0 (m, 2H), 3.1-3.85 (m, 63H), 2.5 (s, 3H),
32 0.6-1.8 (m, 135H).

-34-

01 Example 4

02
03 Preparation of α -(4-Methylsulfonylbenzoyl)-
04 ω -4-dodecylphenoxy poly(oxybutylene)



10 4-Methylsulfonylbenzoyl chloride (12.8 grams, from
11 Example 2) was combined with 98.2 grams of α -hydroxy- ω -4-
12 dodecylphenoxy poly(oxybutylene) having an average of
13 22 oxybutylene units (prepared essentially as described in
14 Example 6 of U.S. Patent No. 4,160,648) and 500 mL of
15 anhydrous toluene. Triethylamine (7.8 mL) and
16 4-dimethylamino pyridine (3.24 grams) were then added and
17 the resulting mixture was heated to reflux under nitrogen
18 for 16 hours. The reaction was cooled to room temperature
19 and diluted with 1 liter of diethyl ether. The organic
20 layer was then washed with 1% aqueous hydrochloric acid,
21 twice with saturated aqueous sodium bicarbonate solution,
22 and once with saturated aqueous sodium chloride. The
23 organic layer was then dried over anhydrous magnesium
24 sulfate, filtered and the solvents removed in vacuo to yield
25 101.6 grams of the desired product as a yellow oil. The oil
26 was chromatographed on silica gel, eluting with hexane/ethyl
27 acetate/ethanol (90:8:2) to afford 73.8 grams of the desired
28 product as a yellow oil. The product had an average of
29 22 oxybutylene units. ^1H NMR (CDCl_3) δ 8.25, 8.0 (AB
30 quartet, 4H), 7.1-7.3 (m, 2H), 6.75-6.95 (m, 2H), 5.1-5.3
31 (m, 1H), 3.85-4.0 (m, 2H), 3.1-3.85 (m, 63H), 3.1 (s, 3H),
32 0.6-1.8 (m, 135H).

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01

02

03

Preparation of Polyisobutyl-4-methylthiobenzoate

04

05 To a flask equipped with a mechanical stirrer, thermometer,
06 Dean-Stark trap, reflux condensor and nitrogen inlet was
07 added 35.0 grams of polyisobutanol (molecular weight average
08 984, prepared via hydroformylation of Amoco H-100
09 polyisobutene), 10.12 grams of 4-methylthiobenzoic acid and
10 0.86 grams of p-toluenesulfonic acid. The mixture was
11 stirred at 130°C for 16 hours, cooled to room temperature,
12 and diluted with 500 mL of diethyl ether. The organic phase
13 was washed twice with saturated aqueous sodium bicarbonate
14 solution, and once with saturated aqueous sodium chloride.
15 The organic layer was then dried over anhydrous magnesium
16 sulfate, filtered and the solvents removed in vacuo to yield
17 34.2 grams of the desired product as a yellow oil. The oil
18 was chromatographed on silica gel, eluting with hexane/ethyl
19 acetate/ethanol (90:8:2) to afford 27.5 grams of the desired
20 product as a yellow oil. IR (neat) 1722 cm⁻¹; ¹H NMR (CDCl₃)
21 δ 7.85, 7.25 (AB quartet, 4H), 4.3 (t, 2H), 2.5 (s, 3H),
22 0.6-1.8 (m, 137H).

23

24

25

Example 6

26

Preparation of Polyisobutyl-4-methylsulfonylbenzoate

27

28 To a flask equipped with a mechanical stirrer, thermometer,
29 Dean-Stark trap, reflux condensor and nitrogen inlet was
30 added 21.0 grams of polyisobutanol (molecular weight average
31 984, prepared via hydroformylation of Amoco H-100
32 polyisobutene), 7.23 grams of 4-methylsulfonylbenzoic acid
33 and 0.52 grams of p-toluenesulfonic acid. The mixture was
34

-36-

01 stirred at 130°C for 16 hours, cooled to room temperature,
 02 and diluted with 500 mL of diethyl ether. The organic phase
 03 was washed twice with saturated aqueous sodium bicarbonate
 04 solution, and once with saturated aqueous sodium chloride.
 05 The organic layer was then dried over anhydrous magnesium
 06 sulfate, filtered and the solvents removed in vacuo to yield
 07 14.5 grams of the desired product as a brown oil. The oil
 08 was chromatographed on silica gel, eluting with hexane/ethyl
 09 acetate/ethanol (90:8:2) to afford 8.7 grams of the desired
 10 product as a yellow oil. IR (neat) 1729 cm⁻¹; ¹H NMR (CDCl₃)
 11 δ 8.5, 8.1 (AB quartet, 4H), 4.35 (t, 2H), 3.1 (s, 3H),
 12 0.6-1.8 (m, 137H).

13

Example 7

14

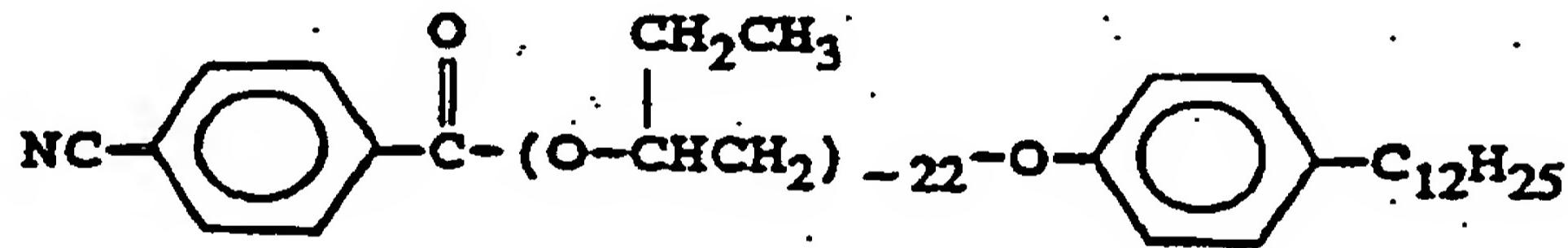
Preparation of

15

α-(4-Cyanobenzoyl)-ω-4-dodecylphenoxy poly(oxybutylene)

16

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24 4-Cyanobenzoyl chloride (3.31 grams) was combined with
 25 36.0 grams of α-hydroxy-ω-4-dodecylphenoxy poly(oxybutylene)
 26 having an average of 22 oxybutylene units (prepared
 27 essentially as described in Example 6 of U.S. Patent
 28 No. 4,160,648) and 250 mL of anhydrous toluene.
 29 Triethylamine (3.9 mL) and 4-dimethylamino pyridine
 30 (1.5 grams) were then added and the resulting mixture was
 31 heated to reflux under nitrogen for 16 hours. The reaction
 32 was cooled to room temperature and diluted with 500 mL of
 33 hexane. The organic layer was then washed with 1% aqueous
 34 hydrochloric acid, twice with saturated aqueous sodium

-37-

01 bicarbonate solution, and once with saturated aqueous sodium
02 chloride. The organic layer was then dried over anhydrous
03 magnesium sulfate, filtered and the solvents removed
04 in vacuo to yield 44.5 grams of the desired product as a
05 brown oil. The oil was chromatographed on silica gel,
06 eluting with hexane/ethyl acetate/ethanol (70:25:5) to
07 afford 22.0 grams of the desired product as a yellow oil.
08 The product had an average of 22 oxybutylene units. IR
09 (neat) 2233, 1722 cm⁻¹; ¹H NMR (CDCl₃) δ 8.2, 7.75 (AB
10 quartet, 4H), 7.1-7.3 (m, 2H), 6.75-6.95 (m, 2H), 5.1-5.3
11 (m, 1H), 3.85-4.0 (m, 2H), 3.1-3.85 (m, 63H), 0.6-1.8 (m,
12 135H).

13

Example 8

14

15

Preparation of mono-Methyl terephthaloyl chloride

16

17

18 To a flask equipped with a magnetic stirrer, reflux
19 condensor and nitrogen inlet was added 36.0 grams of
20 mono-methyl terephthalic acid and 204.6 mL of thionyl
21 chloride. The reaction was heated to reflux for 16 hours
22 and the solvents removed in vacuo to yield 40.0 grams of the
23 desired acid chloride as a white solid.

24

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Example 9

26

27

Preparation of α-(4-Carbomethoxybenzoyl)-ω-
4-dodecylphenoxy poly(oxybutylene)

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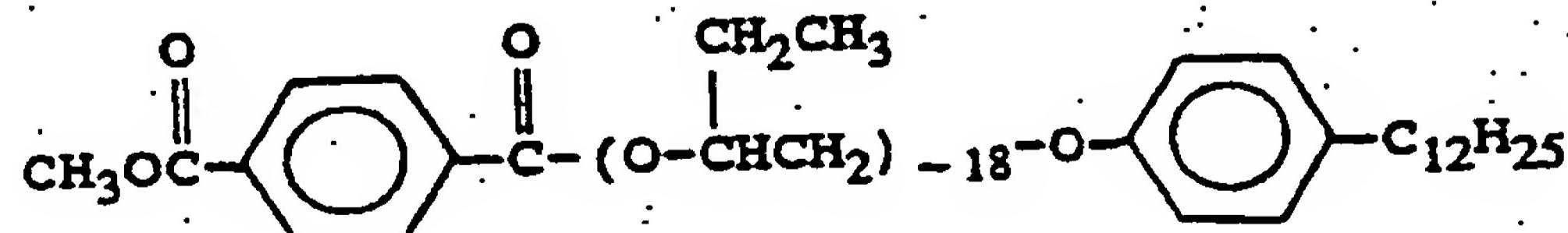
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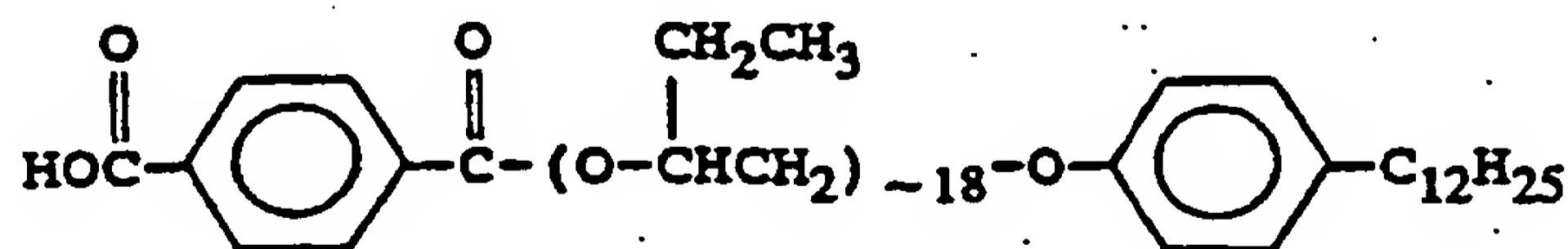


-38-

01 mono-Methyl terephthaloyl chloride (40.0 grams, from
02 Example 8) was combined with 359.0 grams of α -hydroxy- ω -4-
03 dodecylphenoxy poly(oxybutylene) having an average of
04 18 oxybutylene units (prepared essentially as described in
05 Example 6 of U.S. Patent No. 4,160,648) and 500 mL of
06 anhydrous toluene. Triethylamine (30.7 mL) and
07 4-dimethylamino pyridine (12.2 grams) were then added and
08 the resulting mixture was heated to reflux under nitrogen
09 for 16 hours. The reaction was cooled to room temperature
10 and diluted with 1.5 liters of hexane. The organic layer
11 was then washed with 1% aqueous hydrochloric acid, twice
12 with saturated aqueous sodium bicarbonate solution, and once
13 with saturated aqueous sodium chloride. The organic layer
14 was then dried over anhydrous magnesium sulfate, filtered
15 and the solvents removed in vacuo to yield 400 grams of the
16 desired product as a brown oil. The oil was chromatographed
17 on silica gel, eluting with hexane/diethyl ether (1:1) to
18 afford 220 grams of the desired product as a yellow oil.
19 The product had an average of 18 oxybutylene units. IR
20 (neat) 1722 cm^{-1} ; ^1H NMR (CDCl_3) δ 8.1 (s, 4H), 7.1-7.3 (m,
21 2H), 6.75-6.95 (m, 2H), 5.1-5.25 (m, 1H), 3.85-4.0 (m, 2H),
22 3.8 (s, 3H), 3.1-3.85 (m, 51H), 0.6-1.8 (m, 115H).

Example 10

Preparation of α -(4-Carboxybenzoyl)- ω -4-dodecylphenoxy poly(oxybutylene)

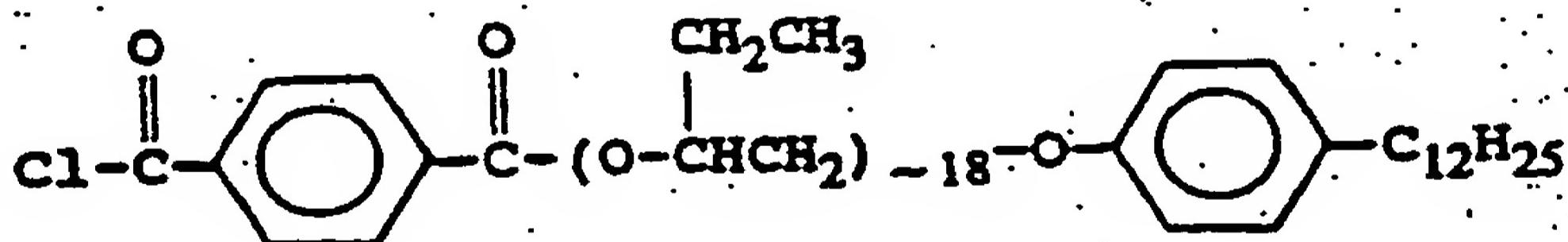


-39-

01 To a flask equipped with a magnetic stirrer and nitrogen
02 inlet was added α -(4-carbomethoxybenzoyl)- ω -4-
03 dodecylphenoxy poly(oxybutylene) (18 grams, from Example 9),
04 10% aqueous sodium hydroxide (w/w, 4.0 grams), and
05 tetrahydrofuran (10 mL). The reaction was stirred at room
06 temperature for 16 hours and the solvents removed in vacuo.
07 The residue was diluted with 100 mL of water and acidified
08 to pH 3 with concentrated hydrochloric acid. The aqueous
09 layer was extracted three times with diethyl ether. The
10 combined diethyl ether layers were dried over anhydrous
11 magnesium sulfate, filtered and the solvents removed
12 in vacuo to yield 13.8 grams as an oil. The oil was
13 chromatographed on silica gel, eluting with hexane/diethyl
14 ether (1:1), followed by hexane/diethyl ether/acetic acid
15 (50:45:5) to afford 5.8 grams of the desired product. The
16 product had an average of 18 oxybutylene units. IR (neat)
17 1722 cm⁻¹; ¹H NMR (CDCl₃) δ 8.05 (s, 4H); 7.0-7.2 (m, 2H),
18 6.7-6.9 (m, 2H), 5.1-5.25 (m, 1H), 3.85-4.0 (m, 2H),
19 3.1-3.85 (m, 51H), 0.6-1.8 (m, 115H).

20
21 Example 11

22
23 Preparation of α -(mono-Terephthaloyl)- ω -
24 4-dodecylphenoxy poly(oxybutylene) chloride



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29
30 To a flask equipped with a magnetic stirrer and a drying
31 tube was added 18.5 grams of α -(4-carboxybenzoyl)- ω -4-
32 dodecylphenoxy poly(oxybutylene), 150 mL of anhydrous diethyl
33 ether, and then 3 mL of oxalyl chloride. The resulting
34

-40-

01 mixture was stirred at room temperature for 16 hours and
02 then the solvents removed in vacuo to yield 18.5 grams of
03 the desired acid chloride.

04

05

Example 12

06

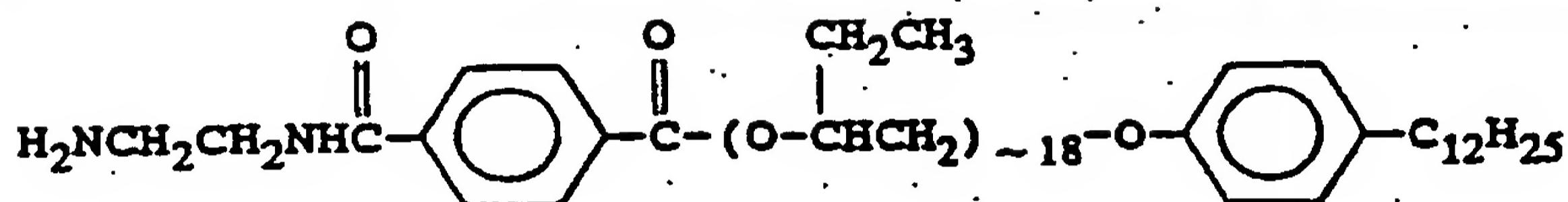
07

Preparation of α -(4-Aminoethylcarbamylbenzoyl)- ω -4-dodecylphenoxy poly(oxybutylene)

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To a flask equipped with a magnetic stirrer, thermometer, addition funnel and nitrogen inlet was added ethylenediamine (4.4 mL) and 25 mL of diethyl ether. The contents of the flask were cooled to 0°C and α -(mono-terephthaloyl)- ω -4-dodecylphenoxy poly(oxybutylene) chloride (18.5 grams, prepared as in Example 11) dissolved in 50 mL of diethyl ether was added dropwise. The reaction was stirred at room temperature for 16 hours, diluted with diethyl ether (200 mL), washed twice with saturated aqueous sodium bicarbonate solution, twice with water, and once with saturated aqueous sodium chloride. The organic layer was then dried over anhydrous magnesium sulfate, filtered and the solvents removed in vacuo to yield 22.6 grams of product. The oil was chromatographed on silica gel, eluting with hexane/diethyl ether/ethanol (70:29:1) to afford 6.5 grams of the desired product as an oil. The product had an average of 18 oxybutylene units. ^1H NMR (CDCl_3) δ 8.1 (s, 4H), 7.1-7.3 (m, 2H), 6.75-6.95 (m, 2H), 5.1-5.25 (m, 1H), 3.85-4.0 (m, 2H), 3.1-3.85 (m, 53H), 2.5-2.7 (m, 2H), 0.6-1.8 (m, 115H).

15

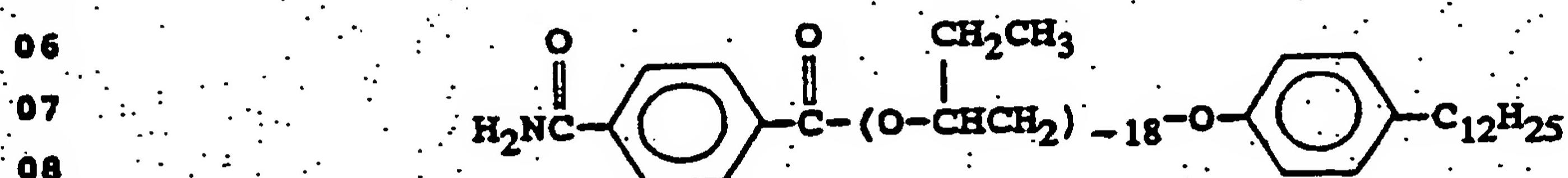
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Example 13.

01
02
03 Preparation of α -(4-Carbamylbenzoyl)- ω -
04 4-dodecylphenoxy poly(oxybutylene)



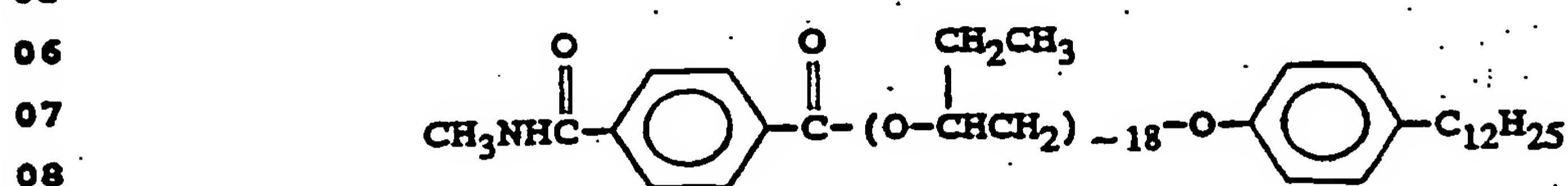
10 To a flask equipped with a magnetic stirrer, addition funnel
11 and nitrogen inlet was added ammonia (12.5 mL of a 2.0 M
12 solution in methanol), dichloromethane (100 mL), and
13 α -(mono-terephthaloyl)- ω -4-dodecylphenoxy poly(oxybutylene)
14 chloride (9.0 grams, prepared as in Example 11). The
15 reaction was stirred at room temperature for 16 hours,
16 diluted with dichloromethane (200 mL), washed twice with
17 saturated aqueous sodium bicarbonate solution, and once with
18 saturated aqueous sodium chloride. The organic layer was
19 then dried over anhydrous magnesium sulfate, filtered and
20 the solvents removed in vacuo to yield 7.1 grams of the
21 desired product as a brown oil. The product had an average
22 of 18 oxybutylene units: IR (neat) 1722, 1682 cm^{-1} ; ^1H NMR
23 (CDCl_3) δ 8.1, 7.8 (AB quartet, 4H), 7.1-7.3 (m, 2H),
24 6.75-6.95 (m, 2H), 5.1-5.25 (m, 1H), 3.85-4.0 (m, 2H),
25 3.1-3.85 (m, 51H), 0.6-1.8 (m, 115H).

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01 Example 14

02
03 Preparation of α -(4-N-Methylcarbamylbenzoyl)- ω -
04 4-dodecylphenoxy poly(oxybutylene)



10 To a flask equipped with a magnetic stirrer, addition funnel
11 and nitrogen inlet was added methylamine (2.2 mL of a
12 40 weight percent solution in water), tetrahydrofuran
13 (75 mL), and α -(mono-terephthaloyl)- ω -4-
14 dodecylphenoxy poly(oxybutylene) chloride (9.0 grams,
15 prepared as in Example 11). The reaction was stirred at
16 room temperature for 16 hours, diluted with diethyl ether
17 (200 mL), washed twice with saturated aqueous sodium
18 bicarbonate solution, and once with saturated aqueous sodium
19 chloride. The organic layer was then dried over anhydrous
20 magnesium sulfate, filtered and the solvents removed
21 in vacuo. The oil was chromatographed on silica gel,
22 eluting with hexane/diethyl ether/ethanol (70:29:1) to
23 afford 6.5 grams of the desired product as an oil. The
24 product had an average of 18 oxybutylene units. ^1H NMR
25 (CDCl_3) δ 8.1, 7.8 (AB quartet, 4H), 7.1-7.25 (m, 2H),
26 6.75-6.95 (m, 2H), 6.55-6.75 (bs, 1H); 5.1-5.25 (m, 1H),
27 3.85-4.0 (m, 2H), 3.1-3.85 (m, 5H), 3.0 (d, 3H), 0.6-1.8
28 (m, 115H).

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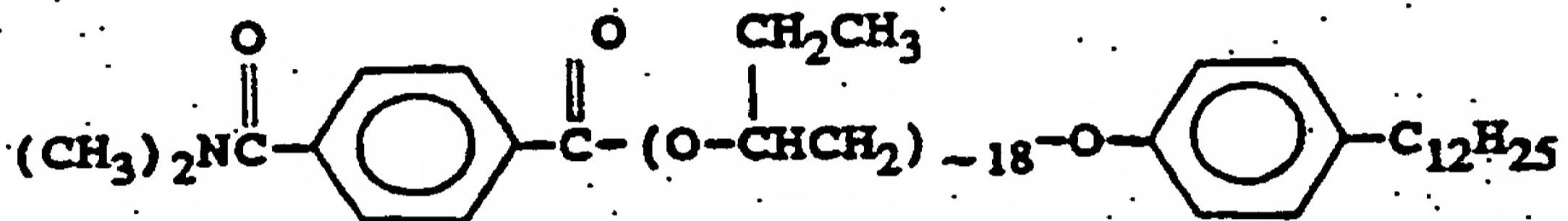
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-43-

01 Example 15

02
03 Preparation of α -(4-N-N-Dimethylcarbamylbenzoyl)- ω -
04 4-dodecylphenoxy poly(oxybutylene)



10 To a flask equipped with a magnetic stirrer, addition funnel
11 and nitrogen inlet was added dimethylamine (4.2 mL of a
12 40 weight percent solution in water), tetrahydrofuran
13 (75 mL), and α -(mono-terephthaloyl)- ω -4-
14 dodecylphenoxy poly(oxybutylene) chloride (12.0 grams,
15 prepared as in Example 11). The reaction was stirred at
16 room temperature for 16 hours, diluted with diethyl ether
17 (200 mL), washed twice with saturated aqueous sodium
18 bicarbonate solution, and once with saturated aqueous sodium
19 chloride. The organic layer was then dried over anhydrous
20 magnesium sulfate, filtered and the solvents removed
21 in vacuo. The oil was chromatographed on silica gel,
22 eluting with hexane/diethyl ether/ethanol (70:29:1) to
23 afford 10.2 grams of the desired product as an oil. The
24 product had an average of 18 oxybutylene units. ^1H NMR
25 (CDCl_3) δ 8.2, 7.5 (AB quartet, 4H), 7.1-7.25 (m, 2H),
26 6.75-6.95 (m, 2H), 5.1-5.25 (m, 1H), 3.85-4.0 (m, 2H),
27 3.1-3.85 (m, 51H), 3.1 (s, 3H), 2.95 (s, 3H), 0.6-1.8 (m,
28 115H).

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01

Comparative Example A

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03

Preparation of

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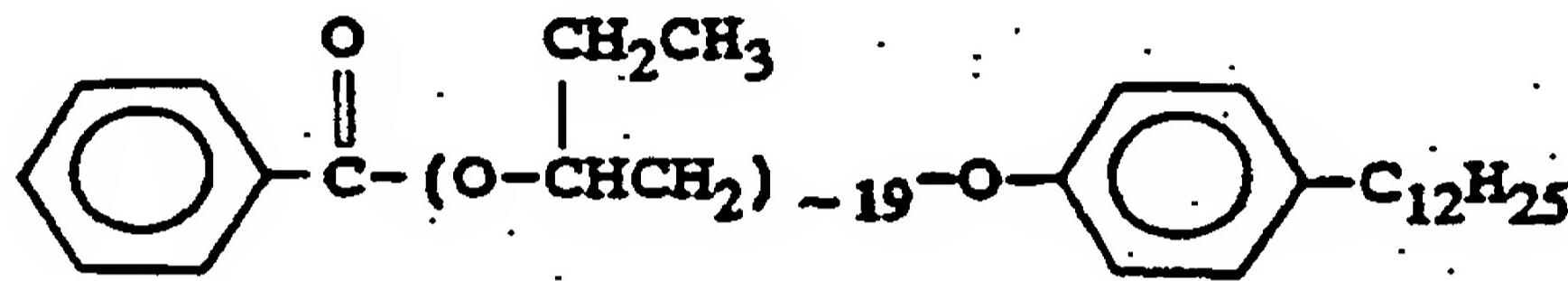
α -(Benzoyl)- ω -4-dodecylphenoxy poly(oxybutylene)

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Benzoyl chloride (2.32 mL) was combined with 35.9 grams of α -hydroxy- ω -4-dodecylphenoxy poly(oxybutylene) having an average of 19 oxybutylene units (prepared essentially as described in Example 6 of U.S. Patent No. 4,160,648) and 250 mL of anhydrous toluene. Triethylamine (3.1 mL) and 4-dimethylamino pyridine (1.22 grams) were then added and the resulting mixture was heated to reflux under nitrogen for 16 hours. The reaction was cooled to room temperature and diluted with 600 mL of diethyl ether. The organic layer was then washed with 1% aqueous hydrochloric acid, twice with saturated aqueous sodium bicarbonate solution, and once with saturated aqueous sodium chloride. The organic layer was then dried over anhydrous magnesium sulfate, filtered and the solvents removed in vacuo to yield 41.3 grams of a yellow oil. The oil was chromatographed on silica gel, eluting with hexane/diethyl ethyl/ethanol (70:25:5) to afford 29.0 grams of the desired product as a light yellow oil. The product had an average of 18 oxybutylene units. IR (neat) 1715 cm^{-1} ; ^1H NMR (CDCl_3) δ 8.1 (d, 2H), 7.5-7.65 (m, 1H), 7.3-7.5 (m, 2H), 7.1-7.25 (m, 2H), 6.75-6.85 (m, 2H), 5.1-5.2 (m, 1H), 3.8-4.0 (m, 2H), 3.1-3.8 (m, 54H), 0.6-1.8 (m, 120H).

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Example 16

Single-Cylinder Engine Test

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05 The test compounds were blended in gasoline and their
06 deposit reducing capacity determined in an ASTM/CFR
07 single-cylinder engine test.

08
09 A Waukesha CFR single-cylinder engine was used. Each run
10 was carried out for 15 hours, at the end of which time the
11 intake valve was removed, washed with hexane and weighed.
12 The previously determined weight of the clean valve was
13 subtracted from the weight of the valve at the end of the
14 run. The differences between the two weights is the weight
15 of the deposit. A lesser amount of deposit indicates a
16 superior additive. The operating conditions of the test
17 were as follows: water jacket temperature 200°F; vacuum of
18 12 in Hg, air-fuel ratio of 12, ignition spark timing of
19 40° BTC; engine speed is 1800 rpm; the crankcase oil is a
20 commercial 30W oil.

21
22 The amount of carbonaceous deposit in milligrams on the
23 intake valves is reported for each of the test compounds in
24 Table I.

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TABLE IIntake Valve Deposit Weight
(in milligrams)

Sample ¹	Run 1	Run 2	Average
Base Fuel	168.0	179.2	173.6
Example 3	46.6	70.7	58.7
Example 4	25.1	24.1	24.6
Example 5	78.4	108.4	93.4
Example 6	82.9	93.9	88.4
Example 7	46.3	64.0	55.2
Example 9	53.1	45.6	49.4
Example 10	46.4	23.0	34.7
Example 12	27.8	26.2	27.0
Example 13	21.0	23.5	22.3
Example 14	17.1	23.3	20.2
Example 15	29.3	35.2	32.3
Comp. Exam. A	201.0	207.4	204.2

¹ At 200 parts per million actives (ppma).

The base fuel employed in the above single-cylinder engine tests was a regular octane unleaded gasoline containing no fuel detergent. The test compounds were admixed with the base fuel to give a concentration of 200 ppma (parts per million actives).

The data in Table I illustrates the significant reduction in intake valve deposits provided by the polyalkyl and poly(oxyalkylene) aromatic esters of the present invention (Examples 3-7, 9-10 and 12-15) compared to the base fuel and the poly(oxyalkylene) aromatic ester of Comparative Example A.

-47-

01. WHAT IS CLAIMED IS:

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03. 1. A compound of the formula:

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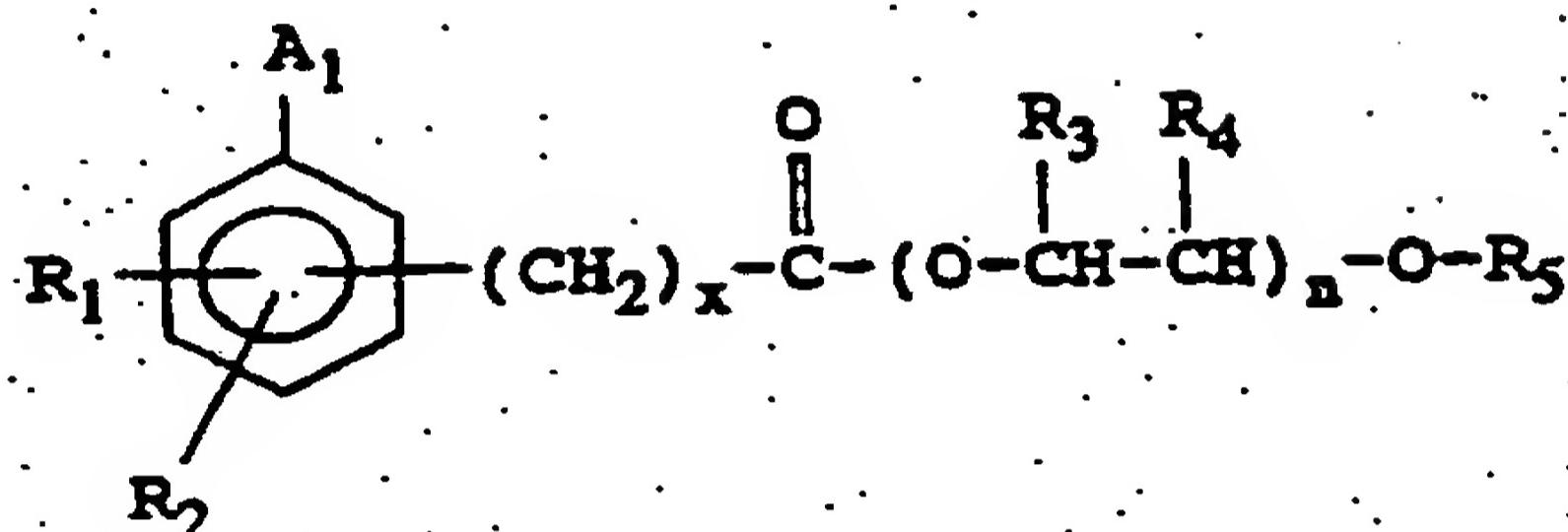
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wherein A_1 is selected from the group consisting of SR^I , SOR^{II} , SO_2R^{III} , wherein R^I , R^{II} and R^{III} are independently lower alkyl of 1 to 6 carbon atoms; SO_3H ; $SO_2NR^{IV}R^{V}$, wherein R^{IV} and R^{V} are independently hydrogen, lower alkyl of 1 to 6 carbon atoms or aminoalkyl of 1 to 6 carbon atoms, provided that R^{IV} and R^{V} may not both be aminoalkyl; CN ; CO_2R^{VI} , wherein R^{VI} is hydrogen or lower alkyl of 1 to 6 carbon atoms; and $C(O)NR^{VII}R^{VIII}$, wherein R^{VII} and R^{VIII} are independently hydrogen, lower alkyl of 1 to 6 carbon atoms or aminoalkyl of 1 to 6 carbon atoms, provided that R^{VII} and R^{VIII} may not both be aminoalkyl;

R_1 and R_2 are independently hydrogen, hydroxy, lower alkyl having 1 to 6 carbon atoms, or lower alkoxy having 1 to 6 carbon atoms;

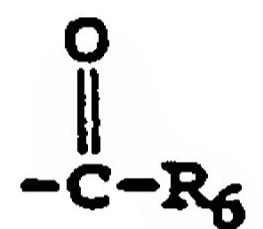
R_3 and R_4 are independently hydrogen or lower alkyl having 1 to 6 carbon atoms and each R_3 and R_4 is independently selected in each $-O-CHR_3-CHR_4-$ unit;

n is an integer from 0 to 100;

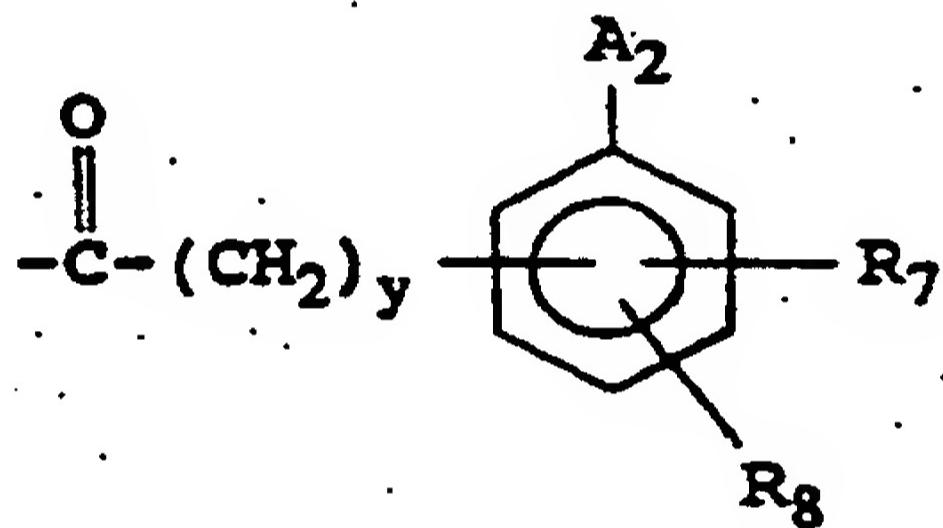
-48-

01 and when n is 0 to 10, then R₅ is a polyalkyl group
02 having an average molecular weight in the range of
03 about 450 to 5,000;

05 and when n is 5 to 100, then R₅ is hydrogen, alkyl
06 having 1 to 100 carbon atoms, phenyl, aralkyl having 7
07 to 100 carbon atoms, alkaryl having 7 to 100 carbon
08 atoms, or an acyl group having the formula:



OR



wherein R₆ is alkyl having 1 to 30 carbon atoms, phenyl, aralkyl having 7 to 36 carbon atoms or alkaryl having 7 to 36 carbon atoms;

21 R₇ and R₈ are independently hydrogen, hydroxy, lower
22 alkyl having 1 to 6 carbon atoms, or lower alkoxy
23 having 1 to 6 carbon atoms;

A₂ is selected from the group consisting of SR^{IX}, SOR^X, SO₂R^{XI}, wherein R^{IX}, R^X and R^{XI} are independently lower alkyl of 1 to 6 carbon atoms; SO₃H; SO₂NR^{XII}R^{XIII}, wherein R^{XII} and R^{XIII} are independently hydrogen or lower alkyl of 1 to 6 carbon atoms; CN; CO₂R^{XIV}, wherein R^{XIV} is hydrogen or lower alkyl of 1 to 6 carbon atoms; and C(O)NR^{XV}R^{XVI}, wherein R^{XV} and R^{XVI} are independently hydrogen or lower alkyl of 1 to 6 carbon atoms;

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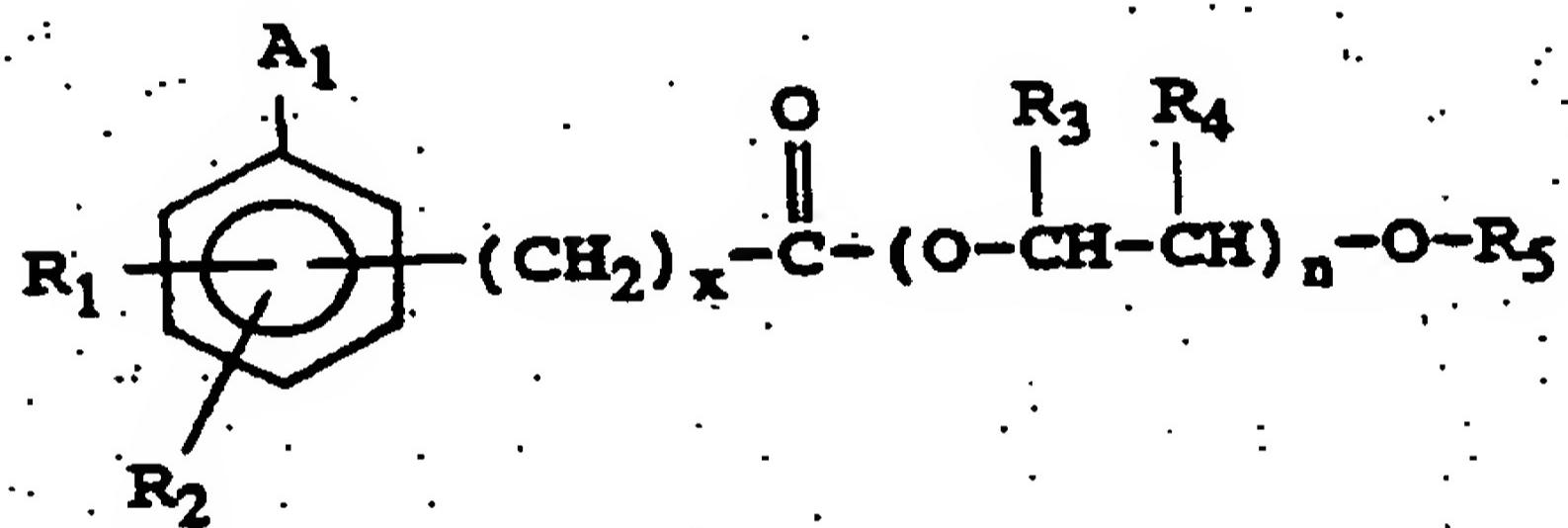
- 01 and x and y are independently integers from 0 to 10;
- 02
- 03 with the proviso that when n and x are both 0, then A₁
- 04 may not be CO₂R^{VI} or C(O)NR^{VII}R^{VIII}.
- 05
- 06 2. The compound according to Claim 1 wherein R₁ is
- 07 hydrogen, hydroxy or lower alkyl having 1 to 4 carbon
- 08 atoms.
- 09
- 10 3. The compound according to Claim 2 wherein R₁ is
- 11 hydrogen or hydroxy.
- 12
- 13 4. The compound according to Claim 3 wherein R₁ is
- 14 hydrogen.
- 15
- 16 5. The compound according to Claim 1 wherein R₂ is
- 17 hydrogen.
- 18
- 19 6. The compound according to Claim 1 wherein x is an
- 20 integer from 0 to 2.
- 21
- 22 7. The compound according to Claim 6 wherein x is 0.
- 23
- 24 8. The compound according to Claim 1 wherein n is an
- 25 integer from 0 to 10.
- 26
- 27 9. The compound according to Claim 8 wherein n is an
- 28 integer from 0 to 5.
- 29
- 30 10. The compound according to Claim 9 wherein n is 0.
- 31
- 32 11. The compound according to Claim 8 wherein R₁ and R₂ are
- 33 both hydrogen and x and n are both 0.
- 34

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- 01 12. The compound according to Claim 8 wherein R₅ is a
- 02 polyalkyl group derived from polypropylene, polybutene,
- 03 or polyalphaolefin oligomers of 1-octene or 1-decene.
- 04
- 05 13. The compound according to Claim 12 wherein R₅ is a
- 06 polyalkyl group derived from polyisobutene.
- 07
- 08 14. The compound according to Claim 1 wherein n is an
- 09 integer from 5 to 100.
- 10
- 11 15. The compound according to Claim 14 wherein n is an
- 12 integer from 8 to 50.
- 13
- 14 16. The compound according to Claim 15 wherein n is an
- 15 integer from 10 to 30.
- 16
- 17 17. The compound according to Claim 14 wherein R₅ is
- 18 hydrogen, alkyl having 1 to 30 carbon atoms or
- 19 alkylphenyl having an alkyl group containing 1 to
- 20 30 carbon atoms.
- 21
- 22 18. The compound according to Claim 1 wherein one of R₃ and
- 23 R₄ is lower alkyl having 1 to 3 carbon atoms and the
- 24 other is hydrogen.
- 25
- 26 19. The compound according to Claim 18 wherein one of R₃
- 27 and R₄ is methyl or ethyl and the other is hydrogen.
- 28
- 29 20. The compound according to Claim 14 wherein R₁ and R₂
- 30 are hydrogen, R₅ is alkylphenyl having an alkyl group
- 31 containing 4 to 12 carbon atoms, and x is 0.
- 32
- 33
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- 01 21. The compound according to Claim 1 wherein A₁ is
 02 selected from the group consisting of SR^I, SO₂R^{III}, CN,
 03 CO₂R^{VI} and C(O)NR^{VII}R^{VIII}.
- 04
- 05 22. The compound according to Claim 21 wherein A₁ is CO₂R^{VI}
 06 or C(O)NR^{VII}R^{VIII}.
- 07
- 08 23. A fuel composition comprising a major amount of
 09 hydrocarbons boiling in the gasoline or diesel range
 10 and an effective detergent amount of a compound of the
 11 formula:



20 wherein A₁ is selected from the group consisting of
 21 SR^I, SOR^{II}, SO₂R^{III}, wherein R^I, R^{II} and R^{III} are
 22 independently lower alkyl of 1 to 6 carbon atoms; SO₃H;
 23 SO₂NR^{IV}R^V, wherein R^{IV} and R^V are independently
 24 hydrogen, lower alkyl of 1 to 6 carbon atoms or
 25 aminoalkyl of 1 to 6 carbon atoms, provided that R^{IV}
 26 and R^V may not both be aminoalkyl; CN; CO₂R^{VI}, wherein
 27 R^{VI} is hydrogen or lower alkyl of 1 to 6 carbon atoms;
 28 and C(O)NR^{VII}R^{VIII}, wherein R^{VII} and R^{VIII} are independently
 29 hydrogen, lower alkyl of 1 to 6 carbon atoms or
 30 aminoalkyl of 1 to 6 carbon atoms, provided that R^{VII}
 31 and R^{VIII} may not both be aminoalkyl;

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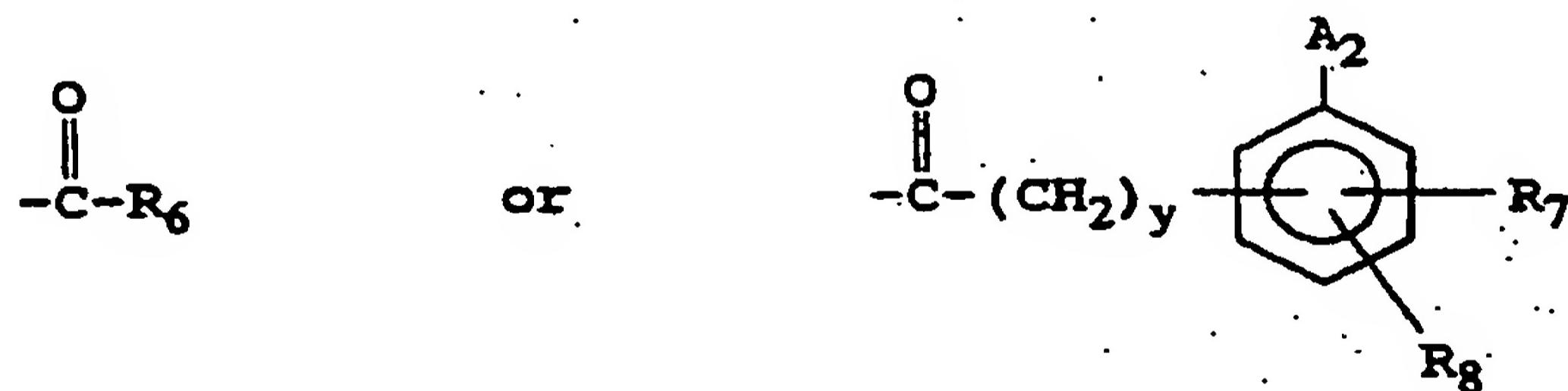
R₁ and R₂ are independently hydrogen, hydroxy, lower alkyl having 1 to 6 carbon atoms, or lower alkoxy having 1 to 6 carbon atoms;

R₃ and R₄ are independently hydrogen or lower alkyl having 1 to 6 carbon atoms and each R₃ and R₄ is independently selected in each -O-CHR₃-CHR₄- unit;

n is an integer from 0 to 100;

and when n is 0 to 10, then R₅ is a polyalkyl group having an average molecular weight in the range of about 450 to 5,000;

and when n is 5 to 100, then R₅ is hydrogen, alkyl having 1 to 100 carbon atoms, phenyl, aralkyl having 7 to 100 carbon atoms, alkaryl having 7 to 100 carbon atoms, or an acyl group having the formula:



wherein R₆ is alkyl having 1 to 30 carbon atoms, phenyl, aralkyl having 7 to 36 carbon atoms or alkaryl having 7 to 36 carbon atoms;

31 R₇ and R₈ are independently hydrogen, hydroxy, lower
32 alkyl having 1 to 6 carbon atoms, or lower alkoxy
33 having 1 to 6 carbon atoms;

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- 01 A₂ is selected from the group consisting of SR^{IX}, SOR^X,
02 SO₂R^{XI}, wherein R^{IX}, R^X and R^{XI} are independently lower
03 alkyl of 1 to 6 carbon atoms; SO₃H; SO₂NR^{XII}R^{XIII}, wherein
04 R^{XII} and R^{XIII} are independently hydrogen or lower alkyl
05 of 1 to 6 carbon atoms; CN; CO₂R^{XIV}, wherein R^{XIV} is
06 hydrogen or lower alkyl of 1 to 6 carbon atoms; and
07 C(O)NR^{XV}R^{XVI}, wherein R^{XV} and R^{XVI} are independently
08 hydrogen or lower alkyl of 1 to 6 carbon atoms;
09
10 and x and y are independently integers from 0 to 10;
11
12 with the proviso that when n and x are both 0, then A₁
13 may not be CO₂R^{VI} or C(O)NR^{VII}R^{VIII}.
14
15 24. The fuel composition according to Claim 23 wherein R₁
16 is hydrogen, hydroxy or lower alkyl having 1 to
17 4 carbon atoms.
18
19 25. The fuel composition according to Claim 24 wherein R₁
20 is hydrogen or hydroxy.
21
22 26. The fuel composition according to Claim 25 wherein R₁
23 is hydrogen.
24
25 27. The fuel composition according to Claim 23 wherein R₂
26 is hydrogen.
27
28 28. The fuel composition according to Claim 23 wherein x is
29 an integer from 0 to 2.
30
31 29. The fuel composition according to Claim 28 wherein x is
32 0.

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- 01 30. The fuel composition according to Claim 23 wherein n is
02 an integer from 0 to 10.
- 03
- 04 31. The fuel composition according to Claim 30 wherein n is
05 an integer from 0 to 5.
- 06
- 07 32. The fuel composition according to Claim 31 wherein n is
08 0.
- 09
- 10 33. The fuel composition according to Claim 30 wherein R₁
11 and R₂ are both hydrogen and x and n are both 0.
- 12
- 13 34. The fuel composition according to Claim 30 wherein R₅
14 is a polyalkyl group derived from polypropylene,
15 polybutene, or polyalphaolefin oligomers of 1-octene or
16 1-decene.
- 17
- 18 35. The fuel composition according to Claim 34 wherein R₅
19 is a polyalkyl group derived from polyisobutene.
- 20
- 21 36. The fuel composition according to Claim 23 wherein n is
22 an integer from 5 to 100.
- 23
- 24 37. The fuel composition according to Claim 36 wherein n is
25 an integer from 8 to 50.
- 26
- 27 38. The fuel composition according to Claim 37 wherein n is
28 an integer from 10 to 30.
- 29
- 30 39. The fuel composition according to Claim 36 wherein R₅
31 is hydrogen, alkyl having 1 to 30 carbon atoms or
32 alkylphenyl having an alkyl group containing 1 to
33 30 carbon atoms.
- 34

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01 40. The fuel composition according to Claim 23 wherein one
 02 of R₃ and R₄ is lower alkyl having 1 to 3 carbon atoms
 03 and the other is hydrogen.

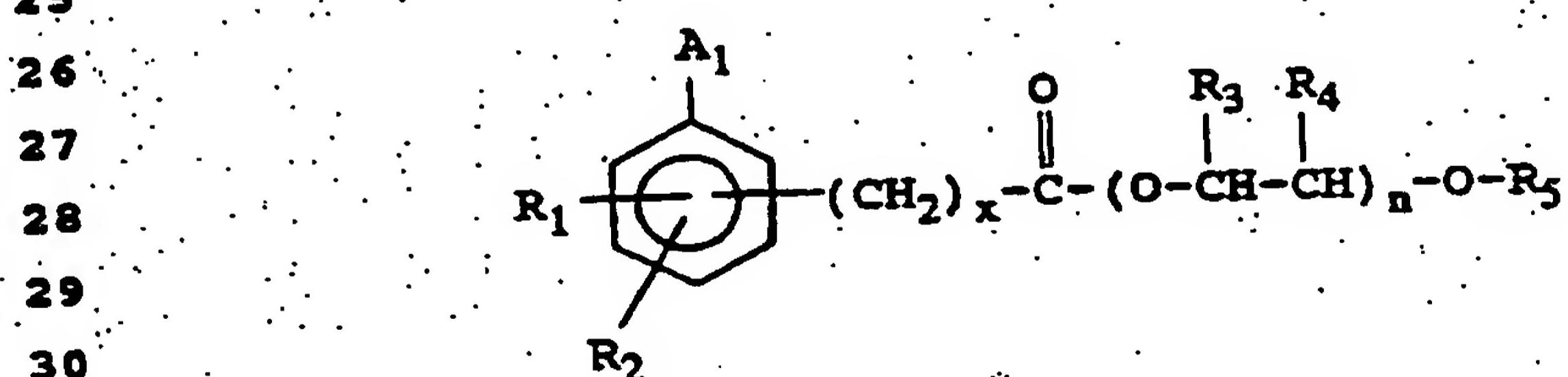
04
 05 41. The fuel composition according to Claim 40 wherein one
 06 of R₃ and R₄ is methyl or ethyl and the other is
 07 hydrogen.

08
 09 42. The fuel composition according to Claim 36 wherein R₁
 10 and R₂ are hydrogen, R₅ is alkylphenyl having an alkyl
 11 group containing 4 to 12 carbon atoms, and x is 0.

12
 13 43. The fuel composition according to Claim 23 wherein A₁
 14 is selected from the group consisting of SR^I, SO₂R^{III},
 15 CN, CO₂R^{VI} and C(O)NR^{VII}R^{VIII}.

16
 17 44. The fuel composition according to Claim 43 wherein A₁
 18 is CO₂R^{VI} or C(O)NR^{VII}R^{VIII}.

19
 20 45. A fuel concentrate comprising an inert stable
 21 oleophilic organic solvent boiling in the range of from
 22 about 150°F to 400°F and from about 10 to about
 23 70 weight percent of a compound of the formula:



32 wherein A₁ is selected from the group consisting of
 33 SR^I, SOR^{II}, SO₂R^{III}, wherein R^I, R^{II} and R^{III} are
 34

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01 independently lower alkyl of 1 to 6 carbon atoms; SO_3H ;
02 $\text{SO}_2\text{NR}^{\text{IV}}\text{R}^{\text{V}}$, wherein R^{IV} and R^{V} are independently
03 hydrogen, lower alkyl of 1 to 6 carbon atoms or
04 aminoalkyl of 1 to 6 carbon atoms, provided that R^{IV}
05 and R^{V} may not both be aminoalkyl; CN ; $\text{CO}_2\text{R}^{\text{VI}}$, wherein
06 R^{VI} is hydrogen or lower alkyl of 1 to 6 carbon atoms;
07 and $\text{C}(\text{O})\text{NR}^{\text{VII}}\text{R}^{\text{VIII}}$, wherein R^{VII} and R^{VIII} are independently
08 hydrogen, lower alkyl of 1 to 6 carbon atoms or
09 aminoalkyl of 1 to 6 carbon atoms, provided that R^{VII}
10 and R^{VIII} may not both be aminoalkyl;
11
12 R_1 and R_2 are independently hydrogen, hydroxy, lower
13 alkyl having 1 to 6 carbon atoms, or lower alkoxy
14 having 1 to 6 carbon atoms;
15
16 R_3 and R_4 are independently hydrogen or lower alkyl
17 having 1 to 6 carbon atoms and each R_3 and R_4 is
18 independently selected in each $-\text{O}-\text{CHR}_3-\text{CHR}_4-$ unit;
19
20 n is an integer from 0 to 100;
21
22 and when n is 0 to 10, then R_5 is a polyalkyl group
23 having an average molecular weight in the range of
24 about 450 to 5,000;
25
26 and when n is 5 to 100, then R_5 is hydrogen, alkyl
27 having 1 to 100 carbon atoms, phenyl, aralkyl having 7
28 to 100 carbon atoms, alkaryl having 7 to 100 carbon
29 atoms, or an acyl group having the formula:
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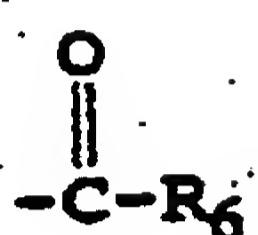
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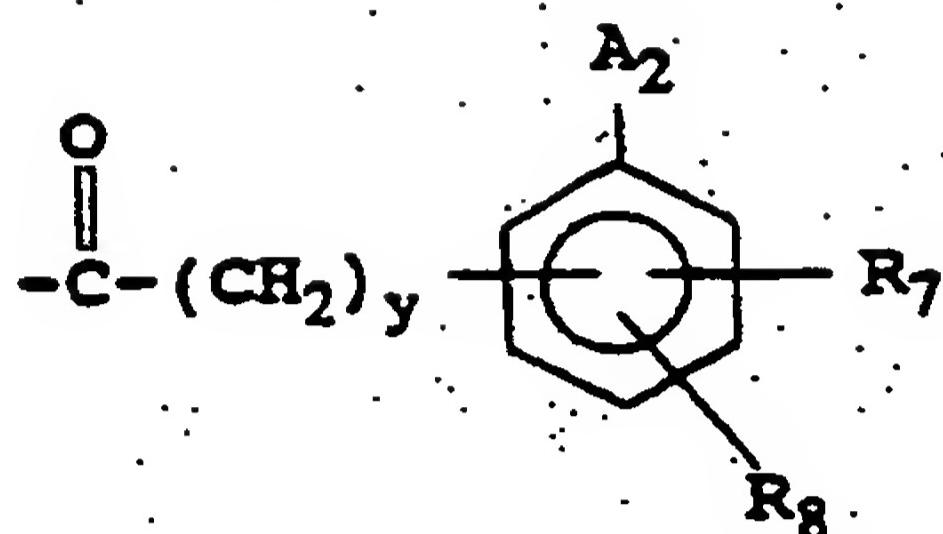
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or



wherein R_6 is alkyl having 1 to 30 carbon atoms, phenyl, aralkyl having 7 to 36 carbon atoms or alkaryl having 7 to 36 carbon atoms;

R_7 and R_8 are independently hydrogen, hydroxy, lower alkyl having 1 to 6 carbon atoms, or lower alkoxy having 1 to 6 carbon atoms;

A_2 is selected from the group consisting of SR^{IX} , SOR^{X} , $\text{SO}_2\text{R}^{\text{XI}}$, wherein R^{IX} , R^{X} and R^{XI} are independently lower alkyl of 1 to 6 carbon atoms; SO_3H ; $\text{SO}_2\text{NR}^{\text{XII}}\text{R}^{\text{XIII}}$, wherein R^{XII} and R^{XIII} are independently hydrogen or lower alkyl of 1 to 6 carbon atoms; CN ; $\text{CO}_2\text{R}^{\text{XIV}}$, wherein R^{XIV} is hydrogen or lower alkyl of 1 to 6 carbon atoms; and $\text{C}(\text{O})\text{NR}^{\text{XV}}\text{R}^{\text{XVI}}$, wherein R^{XV} and R^{XVI} are independently hydrogen or lower alkyl of 1 to 6 carbon atoms;

and x and y are independently integers from 0 to 10;

with the proviso that when n and x are both 0, then A_1 may not be $\text{CO}_2\text{R}^{\text{VI}}$ or $\text{C}(\text{O})\text{NR}^{\text{VII}}\text{R}^{\text{VIII}}$.

46. The fuel concentrate according to Claim 45 wherein R_1 is hydrogen, hydroxy or lower alkyl having 1 to 4 carbon atoms.

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- 01 47. The fuel concentrate according to Claim 46 wherein R₁
02 is hydrogen or hydroxy.
- 03
- 04 48. The fuel concentrate according to Claim 47 wherein R₁
05 is hydrogen.
- 06
- 07 49. The fuel concentrate according to Claim 45 wherein R₂
08 is hydrogen.
- 09
- 10 50. The fuel concentrate according to Claim 45 wherein x is
11 an integer from 0 to 2.
- 12
- 13 51. The fuel concentrate according to Claim 50 wherein x is
14 0.
- 15
- 16 52. The fuel concentrate according to Claim 46 wherein n is
17 an integer from 0 to 10.
- 18
- 19 53. The fuel concentrate according to Claim 52 wherein n is
20 an integer from 0 to 5.
- 21
- 22 54. The fuel concentrate according to Claim 53 wherein n is
23 0.
- 24
- 25 55. The fuel concentrate according to Claim 52 wherein R₁
26 and R₂ are both hydrogen and x and n are both 0.
- 27
- 28 56. The fuel concentrate according to Claim 52 wherein R₅
29 is a polyalkyl group derived from polypropylene,
30 polybutene, or polyalphaolefin oligomers of 1-octene or
31 1-decene.
- 32
- 33
- 34

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- 01 57. The fuel concentrate according to Claim 56 wherein R₅
02 is a polyalkyl group derived from polyisobutene.
- 03
- 04 58. The fuel concentrate according to Claim 45 wherein n is
05 an integer from 5 to 100.
- 06
- 07 59. The fuel concentrate according to Claim 58 wherein n is
08 an integer from 8 to 50.
- 09
- 10 60. The fuel concentrate according to Claim 59 wherein n is
11 an integer from 10 to 30.
- 12
- 13 61. The fuel concentrate according to Claim 58 wherein R₅
14 is hydrogen, alkyl having 1 to 30 carbon atoms or
15 alkylphenyl having an alkyl group containing 1 to
16 30 carbon atoms.
- 17
- 18 62. The fuel concentrate according to Claim 45 wherein one
19 of R₃ and R₄ is lower alkyl having 1 to 3 carbon atoms
20 and the other is hydrogen.
- 21
- 22 63. The fuel concentrate according to Claim 62 wherein one
23 of R₃ and R₄ is methyl or ethyl and the other is
24 hydrogen.
- 25
- 26 64. The fuel concentrate according to Claim 58 wherein R₁
27 and R₂ are hydrogen, R₅ is alkylphenyl having an alkyl
28 group containing 4 to 12 carbon atoms, and x is 0.
- 29
- 30 65. The fuel concentrate according to Claim 45 wherein A₁
31 is selected from the group consisting of SR^I, SO₂R^{III},
32 CN, CO₂R^{VI} and C(O)NR^{VII}R^{VIII}.
- 33
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01 66. The fuel concentrate according to Claim 65 wherein A₁
02 is CO₂R^{VI} or C(O)NR^{VII}R^{VIII}.

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INTERNATIONAL SEARCH REPORT

International application No. PCT/US94/14730

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C10L 1/24, 1/22, 1/18; C07F 9/02

US CL : Please See Extra Sheet

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 44/ 371, 384, 390, 391, 398, 399, 400; 558/ 62, 413, 414, 416; 560/81, 91, 105; 562/52, 55, 56, 57

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 3,288,842 (VERDOL) 29 November 1966, column 1, lines 22-64.	1-22
A	US, A, 3,457,286, (DEXTER ET AL.) 22 July 1969	
X	US, A, 4,349,688, (SANDLER) 14 September 1982, see entire document	1-8, 14-17, 21, 22 9-13, 18-20
Y	US, A, 5,024,678, (MERTENS-GOTTSELIG ET AL.) 18 June 1991, column 1, line 35 to column 2, line 40.	1-66
P, Y	US, A, 5,366,519, (CHERPECK) 22 November 1994, see entire document.	1-66

 Further documents are listed in the continuation of Box C. See patent family annex.

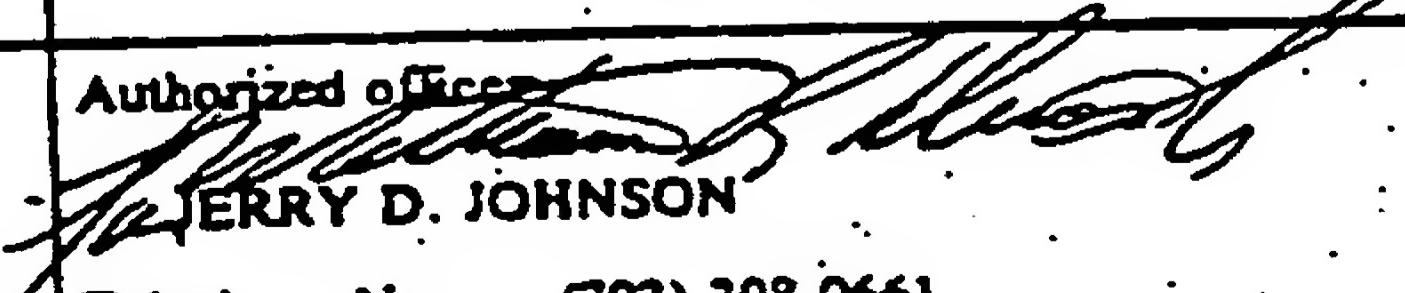
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E earlier document published on or after the international filing date	..	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	..	document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means		
P document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

21 MARCH 1995

Date of mailing of the international search report

06 APR 1995

Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer  JERRY D. JOHNSON Telephone No. (703) 308-0661
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Form PCT/ISA/210 (second sheet)(July 1992)*

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/14730

A. CLASSIFICATION OF SUBJECT MATTER:
US CL :

44/ 371, 384, 390, 391, 398, 399, 400; 558/ 62, 413, 414, 416; 560/81, 91, 105; 562/52, 55, 56, 57

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